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FUEL MICROEMULSIONS FOR  
JET ENGINE SMOKE REDUCTION

LEVEL II

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combined with the microemulsified fuels. The fuels were tested at the takeoff, climb, cruise and ground idle operating condition, and the exhaust smoke, flame radiation and gaseous emissions were measured. The exhaust smoke and flame radiation were significantly reduced by the additions of alcohols and water to the base fuels. Ethanol was found to be most cost effective because it required the least amount of surfactant, which was the most expensive fuel component. The tendency of the microemulsions to form soot was found to correlate with H/C ratio in the same way as typical petroleum-base fuels. Ferrocene, which is well known for its ability to reduce exhaust smoke, had the same effect on the microemulsions as the base fuels; it did not affect flame radiation. Hydrazine was not an effective additive for reducing exhaust smoke.

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PREFACE

This report was prepared by the Mobile Energy Division, Southwest Research Institute, San Antonio, Texas under Contract No. F08635-79-C-0213 with the Air Force Engineering and Services Center, Tyndall Air Force Base, Florida 32403. Major Joseph A. Martone managed the program for the Air Force Engineering and Services Center. The work was begun on 4 July 1979 and was completed on 15 March 1980. It was performed at the U.S. Army Fuels and Lubricants Research Laboratory, Southwest Research Institute, with the permission of the U.S. Army Mobility Equipment Research and Development Command, Energy and Water Resources Laboratory (DRDME-GL), Fort Belvoir, Virginia.

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This report has been reviewed by the Public Affairs Office and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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## SECTION I

### INTRODUCTION

Soot formation in gas turbine engines has always been a problem of concern to the U.S. Air Force. It is well known that exhaust smoke forms obvious signatures and that the flame radiation from incandescent soot particles reduces the life of combustor liners. However, the most recent problem that has arisen is the control of smoke emissions from jet engine test cell facilities. While it is not legally clear that jet engine test cells are subject to stationary source performance standards, the fact remains that Navy test cells have been cited by state air pollution control officials for violations of plume opacity regulations, justifying concern by the Air Force. This situation threatens to worsen as premium petroleum fuels become less available and force the use of jet fuels with lower hydrogen content (higher aromatics) which have a greater propensity to soot.

A concept of water-in-fuel emulsions for the purpose of reducing smoke emissions from jet engine test cells was developed for the U.S. Naval Air Engineering Center. Both T-63 combustor rig tests(1) and a full-scale J-79 engine test(2) were used to confirm the effectiveness of the concept, e.g., in the J-79 testing, a concentration of 15 percent water reduced the observed Ringleman Number from 2.5 to less than 1.

These water-in-fuel macroemulsions were opaque, milky liquids that were formed by homogenization of a water/fuel/surfactant mixture. The basic problems that were encountered with the water-in-fuel macroemulsions were (1) an energy-intensive mechanical device such as a homogenizer was required for their formation, (2) they had limited stability, and (3) it was necessary to account for their decreased energy density when calibrating the engine.

Recently, methods for creating microemulsions of water-in-fuel and of alcohol-in-fuel were developed by the contractor. Microemulsified fuels form spontaneously by simple mixing of fuel, surfactant, and dispersed phase. In principle, microemulsions are stable indefinitely because of their inherent thermodynamic stability. This class of emulsions then offers a distinct potential for eliminating the first two disadvantages. Alcohol-in-fuel emulsions offer the possibility of at least alleviating the third disadvantage since the alcohol would not reduce the energy density as much as water addition does.

A program was therefore developed to determine if microemulsion concepts could be used as a viable method to reduce exhaust smoke from gas turbine engines. This program consisted of three phases to determine the following:

- (1) Can microemulsions be formulated of water-in-JP-4 and JP-8 and of alcohols-in-JP-4 and JP-8?
- (2) Will these fuel formulations significantly reduce exhaust smoke from a gas turbine combustor?
- (3) What are the limits of the water and alcohol concentrations versus smoke reduction, and are there any synergistic effects with other known and candidate smoke suppressants such as ferrocene and hydrazine, respectively?

Ferrocene is an established smoke suppressant for gas turbines. Hydrazine has not been tested in a gas turbine combustor, but claims(3) have been made that hydrazine reduces smoke in utility-type oil burners.

## SECTION II

### APPROACH

The technical plan shown in Figure 1 consists of three phases. In Phase I, the purpose was to prepare microemulsions of water-in-fuel and alcohols-in-fuel using JP-4 and JP-8 as base fuels. After demonstrating that the microemulsified fuels could be prepared, preliminary testing in a T-63 combustor was undertaken in Phase II to determine whether the water and alcohol additions to the neat JP-4 and JP-8 would significantly reduce the exhaust smoke emissions. Phase III included the determination of dispersed phase concentration dependence, the sensitivity to operating conditions, and the possibility of synergisms with other smoke-suppressant additives (hydrazine and ferrocene). In the case of the metallic additive, ferrocene, tests were made to determine if the additions of water or ethanol to JP-4 and JP-8/ferrocene blends would reduce deposition of iron oxide on engine parts.

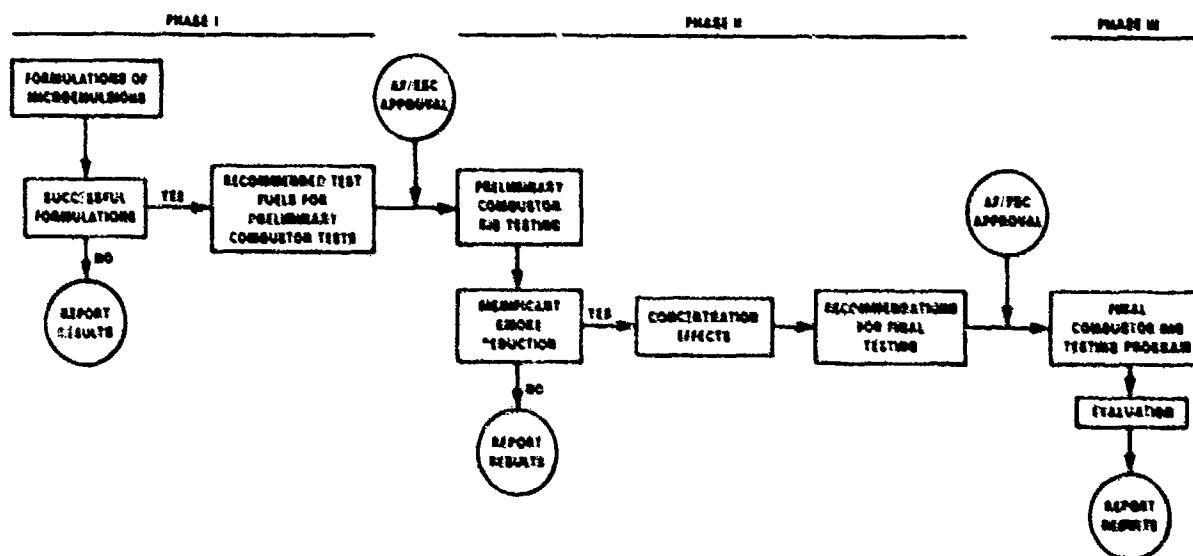


Figure 1. Experimental Approach

## SECTION III

### EXPERIMENTAL FACILITIES AND METHODS

#### General

This work was performed in the U.S. Army Fuels and Lubricants Research Laboratory (AFLRL) with the Army's permission. This facility was specially designed to study fuel-related problems in the operation of turbine engines. The air supply system provides a clean, smooth flow of air to the combustion test cell at rates up to 2.5 lb/sec at pressures to 16 atm and temperatures to 1500°F (uninitiated). Turbine flow meters and strain-gage pressure transducers are used to measure flow properties of the air and fuel. Thermocouples are referenced to a 150°F oven. Data reduction is performed on-line with test summaries available immediately; these summaries provide average flow data as well as standard deviations (typically less than 1 percent of average values), exhaust temperature profiles, and emissions data. Combustion efficiency and fuel/air ratio are calculated from the gaseous emissions.

#### Combustor Rig

The combustor rig shown in Figure 2 is based on engine hardware from the Allison T-63 engine. The burner is a single-can type with a dual-orifice pressure atomizer centered in the dome, as shown in Figure 3. At the burner exit, there is a centerbody that directs the flow into an annulus where the nozzles and turbine blades are normally located. Gas-sampling probes, pressure probes, and thermocouples are arranged circumferentially in one plane of this annulus at various radial positions. Table 1 presents the air flow and fuel flow conditions that were established to correspond with various power points following the guidelines of the manufacturer.

The Air Flow System -- A flow diagram of the air factory is shown in Figure 4. The compressed air for the lab is generated in two stages: two Ingersoll-Rand Pac-Air rotary-screw compressors are connected in parallel, each delivering 1000 SCFM at 100 psig. This air goes through an intercooler and then to a single-cylinder reciprocating compressor where it is compressed to 250 psie. From there, the air passes through an aftercooler, a receiver, and an oil filter before going to the flow controls. The oil carryover is less than 5 ppm. There are suction and discharge bottles on the booster compressor, which, in conjunction with the receiver, were designed on an analog computer by Ingersoll-Rand to eliminate pulsations from the air flow. Pressure fluctuations on the downstream side of the receiver have been measured at less than 0.1 psi peak to peak on a 235 psia flow at a frequency of about 45 Hertz.

The flow control system operates in two parts: one valve is used to provide a pressure drop to the system while a second valve bypasses any excess air flow through an exhaust silencer. The compressors are always operating at full capacity--a method which uses more total energy but eliminates any surging caused by the compressors unloading.

A 3-inch turbine flow meter is used to measure the air flow rate. Because a turbine meter measures volume flow, the pressure and temperature are also sensed at the meter so the flow measurements can be converted to mass flow rate.

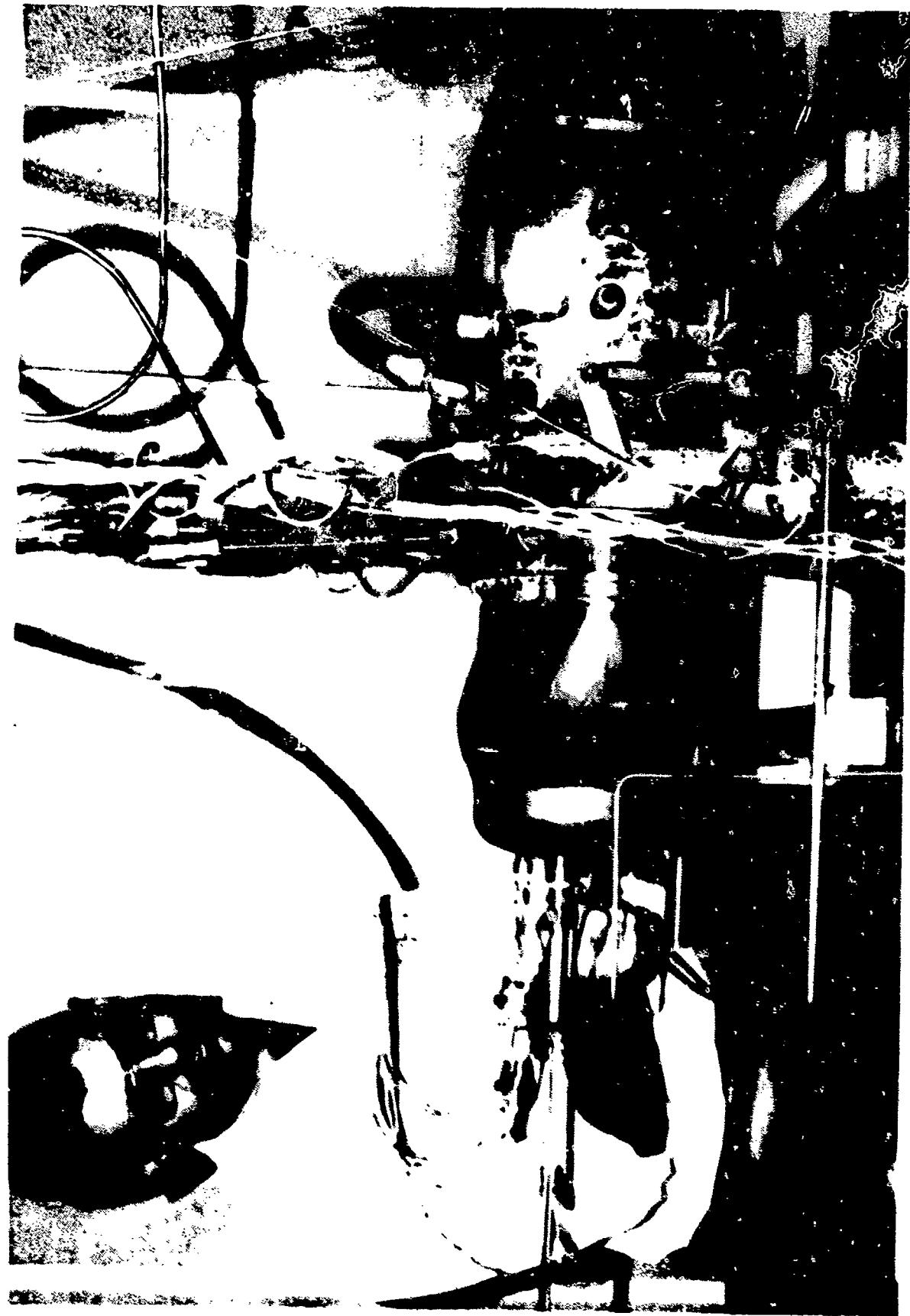


Figure 2. T-63 Combustor Rig

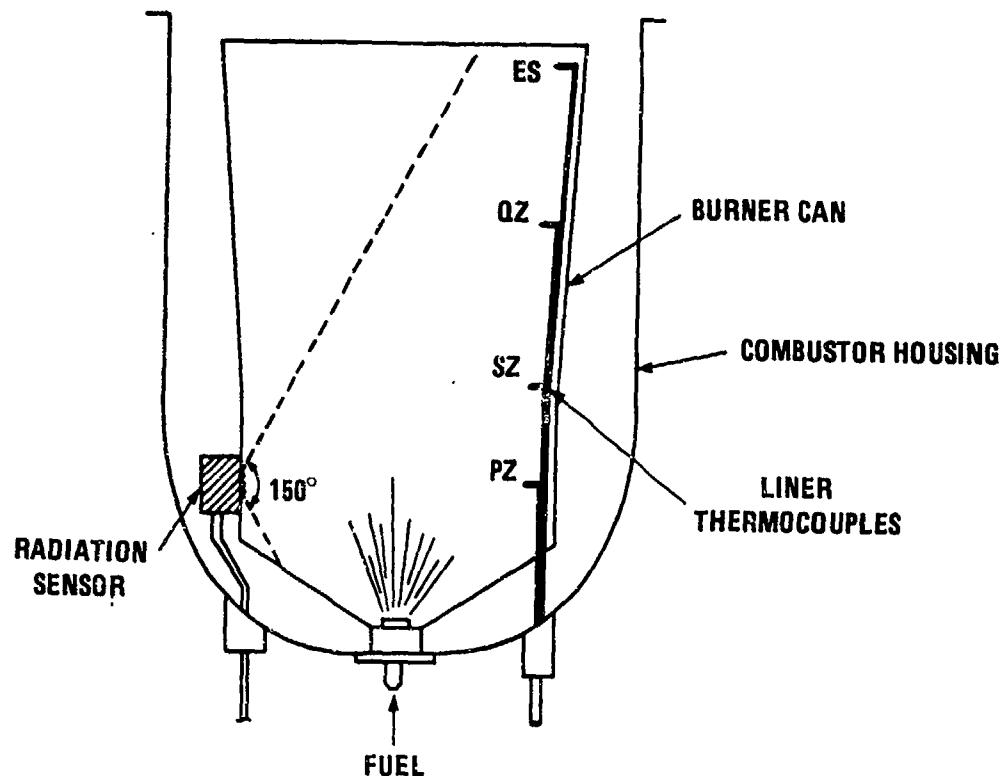


Figure 3. T-63 Combustor

TABLE 1. T-63 COMBUSTOR RIG OPERATING CONDITIONS

Mode	Percent Power	BIP (psia)	BIT (°F)	Wa (lb/s)	Wf (lb/m)	F/A	FF	BOT (°F)
Ground Idle	10	33.4	300	1.40	0.92	0.0109	1.158	1042
Cruise	55	53.6	430	2.06	1.79	0.0145	1.147	1399
Climb	75	60.7	472	2.24	2.23	0.0166	1.123	1559
Takeoff	100	69.2	524	2.42	2.87	0.0198	1.094	1790

Nomenclature

- BIP: Burner inlet pressure
- BIT: Burner inlet temperature
- Wa : Air flow rate
- Wf : Fuel flow rate
- F/A: Fuel/air ratio
- FF : Wa BIT/BIP
- BOT: Typical burner outlet temperature

The air flow then enters a preheater which is capable of heating the flow from roughly 100° to 1550°F. This heater is an indirect, gas-fired system with a counterflow heat exchanger; the air remains unvitiated. The combustion control system was designed in accordance with FIA safety standards to automatic-

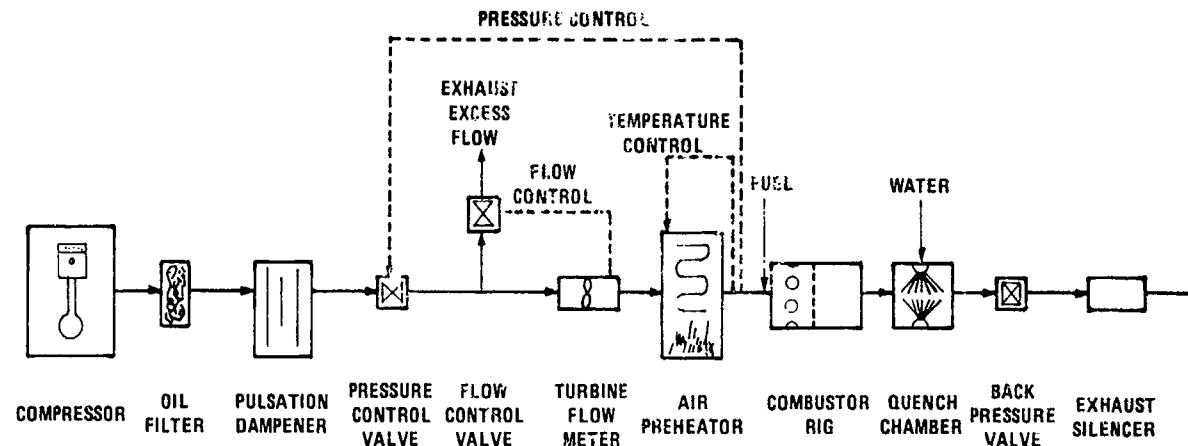


Figure 4. Flow Diagram of Turbine Combustor System

cally shut down the preheater in the event of a malfunction in the fuel supply or temperatures exceeding established limits. The final air temperature is automatically controlled by a Honeywell recorder-controller system which regulates the air/fuel ratio in the combustion chamber and dilutes the hot exhaust gases going to the tube bundle.

The air flow is piped into the test cell and, for all practical purposes, is the same as the air from any turbine compressor. It is essentially pulsation free and oil free, and its moisture content is controlled. The air flow rate, pressure, and temperature are independently adjustable to any values within the operating envelope.

The Fuel Supply System -- The fuel supply system is capable of pumping fluids ranging in properties from JP-4 to No. 5 diesel at flow rates of over 1 gal./min. and pressures up to 1000 psi. For this program, the fuels were forced from drums to the fuel selection manifold system (see Figure 5) with pressurized inert gas. The manifold employs twelve solenoid valves (for 12 fuels). After the manifold, a high-pressure pump delivers fuel to the combustor. The plumbing from the pump to the combustor is stainless steel to facilitate cleaning when special fuels or fuel additives are used.

A turbine flow meter is used to measure the flow rate of the fuel. On starting, a system of valves and bypasses are used to bring the flow rate up to the desired level before introducing it to the combustion chamber. On shutdown, the lines can be drained and purged with an inert gas.

Exhaust System -- A pneumatically-controlled valve is located downstream of the quench section to maintain the pressure in the combustor system. A silencer is used to attenuate the flow noise exhausting from the valve to the atmosphere.

Data Acquisition System -- The data acquisition system is based on a Hewlett-Packard 9820 programmable calculator with associated hardware. Figure 6 shows a flow chart of the system. A digital voltmeter is coupled to a 50-channel scanner which samples the voltage outputs from the various sensor systems and then feeds the corresponding digital values into the calculator. The calculator handles all of the data reduction and any necessary calcula-

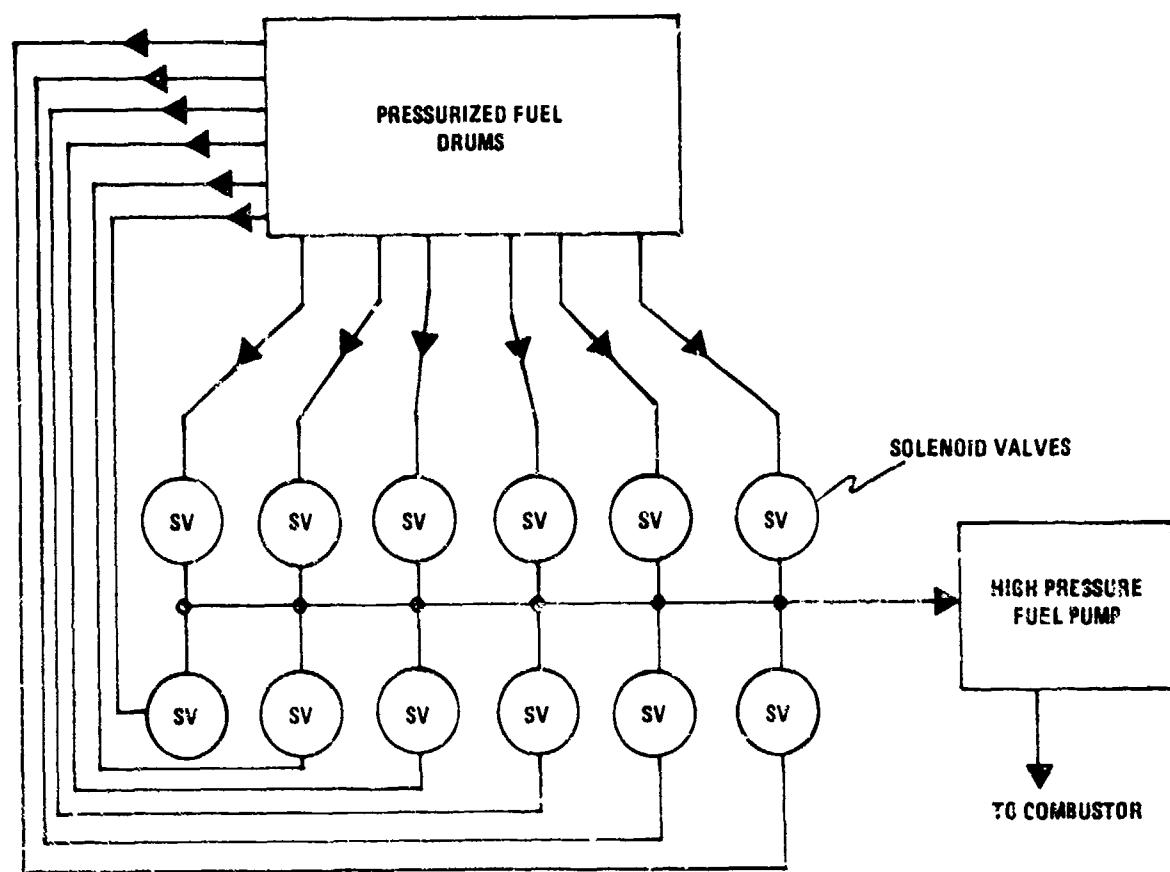


Figure 5. Fuel Selection Manifolding System

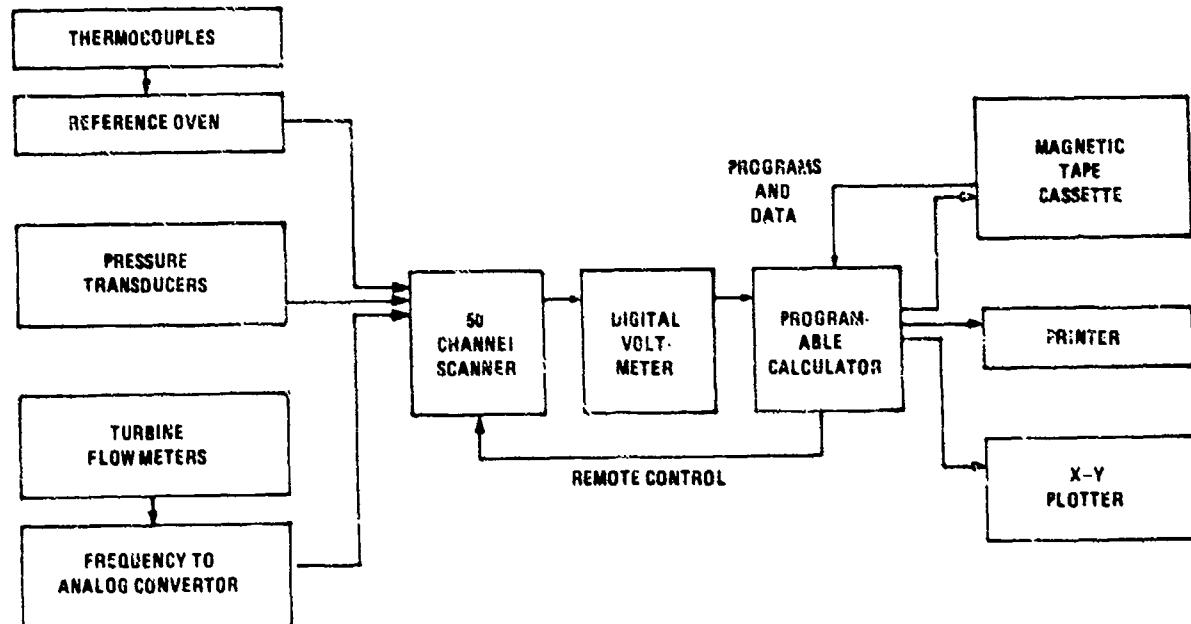


Figure 6. Data Acquisition System

tions, e.g., combustion efficiency, flow factor, and exhaust emissions coefficients. The resulting data are then output in one of three ways:

1. It can be stored on magnetic tape for further reduction at a later time.
2. It can be output graphically on an X-Y plotter.
3. It can be put on a printer along with any appropriate alphanumeric titles or column headings.

The sensing systems consist of strain-gauge pressure transducers, thermocouples, and turbine flowmeters. Regulated power supplies are used with the pressure transducers. A vacuum/pressure reference system is used to calibrate the transducers against a Wallace and Tiernan gauge; use of three-way valves allows this to be done during a test and without disconnecting the transducers. The thermocouples are referenced to a 150°F oven; the unit will handle up to 50 thermocouples of any type including platinum.

Exhaust Analysis Instrumentation -- Exhaust emissions are measured online using the following instruments in accordance with SAE-ARP 1256 with the exception of the NO/NO<sub>x</sub> measurements which are done by chemiluminescence; the instruments and appropriate calibration gases are available essentially 100 percent of the time:

Sample	Instrument	Sensitivity
Carbon Monoxide	Beckman Model 315B NDIR	50 ppm to 16%
Carbon Dioxide	Beckman Model 315B NDIR	300 ppm to 16%
Unburned Hydrocarbons	Beckman Model 402 FID Hydrocarbon Analyzer	0.5 ppm to 10% (CH <sub>4</sub> )
Nitric Oxide	Thermo-Electron 10A Chemiluminescence Analyzer	3 ppm to 10,000 ppm
Total Oxides of Nitrogen	Thermo-Electron 10A Chemiluminescence Analyzer with NO <sub>x</sub> Converter	3 ppm to 10,000 ppm
Oxygen	Beckman Fidelat Oxygen Analyzer	0.1 ppm to 100%

The exhaust sample is brought to the instruments through a 350°F heated Teflon line and then appropriately distributed.

Smoke Analysis System -- The system used for measuring exhaust smoke level is in accordance with the requirements of SAE-ARP 1179. Briefly, a sample of the exhaust is passed through a strip of filter paper. Particulates from the exhaust are trapped on the surface, leaving a spot ranging in grayness from white to black, depending on the sample size and particulate content of the exhaust. The grayness of the spot is evaluated with a reflectometer. The smoke number of each spot is then calculated by:

$$SN = (1 - \frac{R_s}{R_w}) \quad (1)$$

where  $R_s$  and  $R_w$  are the diffuse reflectance of the sample spot and the clean filter paper, respectively. Exhaust samples are taken over a range of sample sizes around  $W/A = 0.023$  pound of sample per square inch of filter area. The resulting smoke numbers are plotted against  $\log (W/A)$ . They are least-squares fitted to a straight line; the interpolated value of  $SN$  at  $W/A = 0.023$  is the reported smoke number for the engine operation condition.

Mass particulate density is calculated from the smoke number according to a semi-logarithm correlation reported by Champagne (4) and curve fitted by Troth, et al., (5) as follows:

$$d_s = K_{1a} \exp(K_{1b} SN) [1 - \exp(-K_2 SN)] + K_{3a} \exp[-K_{3b} (SN - K_{3c})^2] \quad (2)$$

where

$d_s$  = true smoke density, mg/standard cubic meter

$SN$  = smoke number (ARP 1179 Procedure)

$K_{1a}$  = 0.8

$K_{1b}$  = 0.057565

$K_2$  = 0.1335

$K_{3a}$  = 0.0942

$K_{3b}$  = 0.005

$K_{3c}$  = 27.5

Radiation Measurement -- Radiation from the primary zone of the combustor is measured by a water-cooled bolometer-type radiation sensor attached to the side of the burner (see Figure 3). The sensor has a sapphire window and a viewing angle of 150 degrees.

Combustion Efficiency -- Combustion efficiencies are calculated from the exhaust gas analysis according to a relationship developed by Hardin(6):

$$n_b = \left[ 1 - \frac{A \cdot f(UBH) - 121,745 \cdot f(CO) - 38,880 \cdot f(NO) - 14,654 \cdot f(NO_2)}{A \cdot [f(CO_2) + f(CO) + f(UBH)]} \right] \cdot 100\% \quad (3)$$

where  $f(i)$  is the concentration of "i" in the exhaust and  $A$  is a constant based on the heat of combustion and hydrogen/carbon ratio of the fuel.

#### Test Fuels

The test fuels were formulated in the first phase of the program. The objectives were (1) to evaluate several microemulsions of water in JP-4 and JP-8 and alcohols in JP-4 and JP-8 using surfactants that had previously shown promise in similar diesel fuel preparations and (2) to select the most favorable formulations from each of these four categories for combustor testing.

The JP-4 and JP-8 base fuels meeting ASTM specifications were obtained from a local distributor. The JP-4 and JP-8 as received had somewhat low aromatic contents, 15 and 8 percent, respectively, so that for this work aromatics of

an appropriate boiling range were added to them to assure smoke numbers above 30 in the combustor tests. A summary of the fuel properties of JP-4 and JP-8 used in blending the microemulsified fuels is given in Table 2.

TABLE 2. SUMMARY OF FUEL PROPERTIES FOR JP-4 AND JP-8

	<u>JP-4</u>	<u>JP-8</u>
Heat of Combustion, Net (Btu/lb)	18,359	18,390
Carbon, % by Weight	86.45	86.34
Hydrogen, % by Weight	13.54	13.64
Aromatic Ring Carbon by UV		
Single Ring, % by Weight	17.2	19.5
Double Ring, % by Weight	1.1	0.4
Triple Ring, % by Weight	0.0	0.0
HPLC Analysis		
Saturated, % by Weight	---	77.4
Aromatics, % by Weight	---	22.6
FIA Analysis		
Aromatics, % by Volume	23.1	23.6
Olefins, % by Volume	0.6	2.8
Saturates, % by Volume	76.3	73.6
Viscosity at 40°C, (cSt)	0.60	0.96
Flash Point, °F	---	106
Freeze Point, °C	-72	-67
Specific Gravity at 60°F	0.7640	0.7941
API Gravity at 60°F	53.7	46.7
Smoke Point, mm	17.9	19.8
Aniline Point, °C	34.8	50.0
Final Boiling Point, °C	194	256
H/C Atom Ratio	1.879	1.896

Based on previous experience in formulating microemulsions of water, methanol, and ethanol with diesel fuels, eighteen different surfactants (see Table 3) were selected as being potentially successful for JP-4 and JP-8. Of these, the most appropriate surfactants were selected by evaluating approximately fifty test formulations for each JP-4 and JP-8. The laboratory test data on the formulations are present in Tables 4 and 5, and the results are summarized below.

#### A. MICROEMULSIFICATION OF JP-4

(a) Anhydrous ethanol, as expected, is miscible in any proportion with JP-4 without the aid of an emulsifying agent.

(b) Aqueous ethanol, containing about 7 weight percent water, required a surfactant to be dispersible in JP-4. A blend composed of 80 milliliter of JP-4 and 10 milliliter of any one of the 18 surfactants listed in Table 3 could disperse over 100 milliliter of the aqueous ethanol. Of these surfactants, two were randomly selected and were examined at reduced concentrations. These studies showed stable microemulsions were formed by blends containing 2 volume percent of Schercomid SO-Λ® and 18 volume percent of aqueous ethanol

TABLE 3. IDENTIFICATION OF SURFACTANTS

Source	Trade Name*	Reactants		Notes
		Acid (mole)	Amino (mole)	
Scher Chem. Co.	Schercomid SO-A	Oleic Acid (1)	Diethanolamine (1)	
Scher Chem. Co.	Schercomid ODA EA-37	Oleic Acid (1) Oleic Acid (1.025)	Diethanolamine (2)	ODA + 2.5% Oleic Acid
Scher Chem. Co.	EA-12	Oleic Acid (1.050)	Diethanolamine (2)	ODA + 5% Oleic Acid
Scher Chem. Co.	Schercomid OM1	Oleic Acid (1)	1,90-Propylamine (1)	+ 25% Triton X-100
Scher Chem. Co.	Schercomul I	Oleic-and-Palmitic Acids (1)	Diethanolamine (1)	
Scher Chem. Co.	Schercomid SCO-EX	Coconut Oil (1)	Diethanolamine (1)	
Scher Chem. Co.	Schercomid 1-102	Coconut Oil (1.02)	Diethanolamine (1)	+ 25% Triton X-100
Scher Chem. Co.	Schercomul G	poly-Ethoxydodecylphenol		
Clintwood Chem. Co.	Product LT10-8-1	Oleic Acid (1)	Diethanolamine (1)	
Clintwood Chem. Co.	Product LT15-3-1	Oleic-and-Linoleic Acids (1)	Diethanolamine (1)	
Clintwood Chem. Co.	Clindrol 200-0	Oleic Acid (1)	Diethanolamine (2)	
Clintwood Chem. Co.	Product LT17-43-1	Oleic Acid (1)	Diethanolamine (2)	
Clintwood Chem. Co.	Clindrol 101 CG	Coconut Oil (1)	Diethanolamine (1)	
Clintwood Chem. Co.	Clindrol 100 CG	Coconut Oil (1)	Diethanolamine (1)	
Clintwood Chem. Co.	Clindrol 200 RC	Coconut Oil (1)	Diethanolamine (2)	
Clintwood Chem. Co.	Clindrol 203 CG	Coconut Oil (1)	Diethanolamine (2)	
Clintwood Chem. Co.	Clindrol 204CGN	Coconut Oil (2)	Diethanolamine (2)	+ Excess fatty acids

Within each Company's products, the listing is from oleophilic to hydrophilic, according to the manufacturer. Coconut oil-derived fatty acids contain C<sub>8</sub> to C<sub>18</sub> acids.

IUPAC name for products such Schercomid SO-A is: N<sub>1</sub>N-bis(2-hydroxyethyl)-oleamide.

\* Schercomid SO-A, Schercomid ODA, EA-37, EA-12, Schercomul I, Schercomid SCO-EX, Schercomid 1-102, and Schercomul G of Scher Chemical Company, and Product LT10-8-1, Clindrol 200-0, Product LT17-43-1, Clindrol 101CG, Clindrol 100CG, Clindrol 200RC, Clindrol 203CG, and Clindrol 204CGN are registered trademarks of Clintwood Chemical Company, and are so recognized whenever used in this publication.

TABLE 4. ALCOHOLIC AND AQUEOUS MICROEMULSIONS IN JP-4

Serial No.	JP-4 ml.	Surfactant Name	Surfactant ml.	Aqueous Ethanol, ml		Abs. Methanol, ml		Aqueous Methanol, ml		Water, ml	
				Min (1) Blend	Max (2) Blend	Min (1) Blend	Max (2) Blend	Min (1) Blend	Max (2) Blend	Min (1) Blend	Max (2) Blend
1	80	SO-A	10	>100	---	>100	---	13.5	---	16.6	1.6
2	80	SO-A	2	---	18	---	---	---	---	---	4.6
3	67	SO-A	3	---	---	30	---	---	---	---	---
4	77	SO-A	3	---	---	20	---	---	---	---	---
5	87	SO-A	3	---	---	10	---	---	---	---	---
6	75	SO-A	10	---	---	---	---	15	---	---	---
7	80	ODA	10	>100	---	>100	---	9.7	---	10.8	2.5
8	80	EA-37	10	>100	---	>100	---	10.0	---	12.5	4.7
9	80	EA-12	10	>100	---	>100	---	10.5	---	12.9	3.9
10	80	OMI	10	>100	---	>100	---	13.8	---	18.0	0.4
11	67	3	3	---	---	30	---	---	---	---	---
12	77	OMI	3	---	---	20	---	---	---	---	---
13	87	OMI	3	---	---	10	---	---	---	---	---
14	75	OMI	10	---	---	---	---	15	---	---	8.5
15	80	I	10	>100	---	>100	---	13.5	---	15.0	1.3
16	80	G	10	>100	---	>100	---	6.5	---	7.1	6.5
17	70	C	10	---	---	---	---	---	---	20	---
18	75	C	10	---	---	---	---	---	---	15	---
19	80	C	10	---	---	---	---	---	---	10	---
20	80	SCO-EX	10	>100	---	>100	---	8.3	---	8.7	7.3
21	80	I-102	10	>100	---	>100	---	5.5	---	8.0	8.5
22	70	I-102	10	---	---	---	---	---	---	20	---
23	75	I-102	10	---	---	---	---	---	---	15	---
24	80	I-102	10	---	---	---	---	---	---	10(3)	---
25	80	10-8-1	10	>100	---	>100	---	14.2	---	15.6	3.2
26	80	10-8-1	10	---	---	---	---	10	---	15.6	7.1
27	80	15-73-1	10	>100	---	>100	---	12.3	---	13.	0.0
28	80	200-0	10	>100	---	>100	---	3.5	---	6.3	2.3
29	80	17-43-1	10	>100	---	>100	---	11.5	---	14.0	1.8
30	65	17-43-1	5	---	30	---	---	---	---	---	4.6
31	70	17-43-1	5	---	25	---	---	---	---	---	---
32	75	17-43-1	5	---	20	---	---	---	---	---	---
33	80	17-43-1	5	---	15(3)	---	---	---	10	---	19.0
34	80	17-43-1	2	---	18	---	---	---	7.3	7.3	46.5
35	67	17-43-1	3	---	---	30	---	---	---	20	---
36	77	17-43-1	3	---	---	20	---	---	---	15	---
37	67	17-43-1	3	---	---	10	---	---	---	10	---
38	80	17-43-1	10	---	---	---	---	7.3	8.3	7.5	7.5
39	80	101CG	10	>100	---	>100	---	6.7	---	7.3	7.5
40	80	100CG	10	>100	---	>100	---	---	---	20	---
41	79	100CG	10	---	---	---	---	---	---	15	---
42	75	100CG	10	---	---	---	---	---	---	10	---
43	80	100CG	10	---	---	---	---	5.8	8.5	1.1	1.2
44	80	200CG	10	>100	---	>100	---	0.3	---	8.5	18.0
45	80	203CG	10	>100	---	>100	---	---	---	15	---
46	75	203CG	10	---	---	---	---	---	---	10	---
47	80	203CG	10	>100	---	>100	---	6.5	7.8	-0-	---
48	80	204CG	10	>100	---	>100	---	---	---	---	---

(1) Amount of alcohol or water to produce slightly hazy mixture.

(2) Amount of alcohol or water to produce phase separation.

(3) Phase separation.

TABLE 5. ALCOHOLIC AND AQUEOUS MICROEMULSIONS IN JP-8

Serial No.	JP-8 #1	Surfactant Name	Aqueous Ethanol, ml			Aqueous Methanol, ml			Aqueous Methanol, ml		
			Min (1) Blend	Max (2) Min (1) Blend	Max (2) Min (1) Blend	Min (1) Blend	Max (2) Min (1) Blend	Max (2) Min (1) Blend	Min (1) Blend	Max (2) Min (1) Blend	Max (2) Min (1) Blend
101	80	SO-A	10	72.0	75.6	22.6	26.5	7.8	—	12.2	—
102	65	SO-A	5	—	30 (3)	—	—	—	—	—	—
103	75	SO-A	5	—	20 (3)	—	—	—	—	—	—
104	67	SO-A	3	—	30 (3)	—	—	—	—	—	—
105	77	SO-A	3	—	20	—	—	—	—	—	—
106	87	SO-A	3	—	10	—	—	—	—	—	—
107	70	SO-A	10	—	—	—	20	—	—	—	—
108	75	SO-A	10	—	—	—	15	—	—	—	—
109	80	SO-A	10	—	—	—	10	—	—	—	—
110	80	SO-A	10	—	—	—	—	—	10	—	—
111	80	ODA	10	23.8	26.1	7.4	8.3	6.2	—	10.4	4.0
112	80	EA-37	10	24.7	26.9	8.5	9.5	1.5	—	6.7	5.5
113	80	EA-12	10	28.8	32.5	9.8	10.7	5.6	—	8.0	6.3
114	80	OMI	10	>100	—	26.8	—	32.3	8.3	—	13.6
115	65	OMI	5	—	30	—	—	—	—	—	—
116	75	OMI	5	—	20	—	—	—	—	—	—
117	85	OMI	5	—	10	—	—	—	—	—	—
118	67	OMI	3	—	10 (3)	—	—	—	—	—	—
119	77	OMI	3	—	10 (3)	—	—	—	—	—	—
120	67	OMI	3	—	10 (1)	—	—	—	—	—	—
121	70	OMI	19	—	—	—	20	—	—	—	—
122	75	OMI	10	—	—	—	15	—	—	—	—
123	80	OMI	10	—	—	—	10	—	—	—	—
124	80	OMI	10	—	—	—	—	—	10	—	—
125	80	I	44.6	—	60.0	16.7	—	18.7	5.8	—	10.5
126	80	C	10	13.3	13.8	4.7	—	6.0	1.8	—	3.9
127	80	SCO-EX	10	17.5	18.8	6.5	—	7.5	4.3	—	6.2
128	70	SCO-EX	10	—	—	—	—	—	—	—	—
129	75	SCO-EX	10	—	—	—	—	—	—	—	—
130	80	SCO-EX	10	—	—	—	—	—	—	—	—
131	80	1-102	10	9.3	11.5	1.6	—	2.8	1.3	—	2.1
132	80	10-8-1	10	40.5	42.8	14.6	—	16.8	6.7	—	10.8
133	80	15-73-1	10	31.0	38.3	13.3	—	14.3	7.8	—	8.7
134	80	200-0	10	13.8	16.3	6.0	—	7.3	5.7	—	5.3
135	80	17-33-1	10	29.8	31.3	11.6	—	12.4	6.9	—	2.9
136	80	101CC	10	16.3	16.7	5.5	—	6.5	4.1	—	6.2
137	75	101CC	10	—	—	—	—	—	—	—	—
138	80	101CC	10	—	—	—	—	—	—	—	—
139	80	100CC	10	14.8	16.5	3.7	—	5.9	2.2	—	6.0
140	80	200AC	10	11.5	12.5	0.8	—	1.5	0.3	—	0.6
141	80	203CC	10	0.0	0.0	0.0	—	0.0	0.0	—	0.0
142	80	204CCW	10	16.5	—	18.5	4.5	—	5.5	1.0	—
										1.5	0.1
										—	0.2

(1) Amount of Alcohol or water to produce slight haze in mixture.

(2) Amount of Alcohol or water to produce phase separation.

(3) Phase separation.

in the JP-4. Also, 5 volume percent of Product 17-43-1 was able to disperse at least 30 volume percent of aqueous ethanol; however, 2 volume percent of this surfactant was insufficient to disperse 18 volume percent of the aqueous ethanol.

(c) Anhydrous methanol in JP-4 reacted similarly to aqueous ethanol in that 10 milliliter of any of the 18 listed surfactants blended with 80 milliliter of JP-4 was able to disperse over 100 milliliter of absolute methanol. Of the 18 surfactants, three were randomly selected and each was tested at a concentration of 3 volume percent. Each of these emulsifying agents (SO-A<sup>①</sup> OMI<sup>①</sup> and 17-43-1) could support at least 30 volume percent of absolute methanol in the JP-4.

(d) Aqueous methanol was found to require a much higher concentration of surfactant. The study indicated 10 volume percent of SG-A<sup>①</sup> or OMI<sup>①</sup> could disperse 15 volume percent of aqueous methanol, while equal volumes of Product 10-8-1 or 17-43-1 were needed to disperse an equal volume of aqueous methanol.

(e) Water could be dispersed in JP-4 with several surfactants. The study showed that 20 volume percent of water could be dispersed with 10 volume percent of Schercomul G<sup>①</sup> or Schercomid 1-102<sup>①</sup> or Clindrol 100 CG<sup>①</sup>. A phenomenon not observed elsewhere was noted in the case of Schercomid 1-102<sup>①</sup>. While 10 volume percent of this surfactant produced clear products with 15 or 20 volume percent of water, phase separation occurred if only 10 volume percent of water was used.

B. MICROEMULSIFICATION OF JP-8 was generally more difficult than microemulsification of JP-4.

(a) Anhydrous ethanol is miscible with JP-8 in any proportion without the use of emulsifying agents.

(b) Aqueous ethanol, containing about 7 weight percent of water, could be dispersed in JP-8 with all but one of the 18 surfactants that worked with JP-4. The most efficient of these surfactants was Schercomid OMI<sup>①</sup> followed by (in decreasing order of efficiency) Schercomid SO-A<sup>①</sup>, Schercomul I<sup>①</sup>, and Product 10-8-1.

(c) Anhydrous methanol can be emulsified in JP-8 most efficiently with Schercomids SO-A<sup>①</sup> and OMI<sup>①</sup> as 10 volume percent of either one of these surfactants is capable in dispersing up to 20 volume percent of absolute methanol.

(d) Aqueous methanol, containing about 7 weight percent of water, could also be emulsified in JP-8 most efficiently with the aid of Schercomids SO-A<sup>①</sup> or OMI<sup>①</sup>. However, the required volumetric ratio of surfactant to aqueous methanol was found to be one-to-one.

(e) Water was microemulsified in JP-8 best by the aid of either Schercomid SCO-EX<sup>①</sup> or by Clindrol 101 CG<sup>①</sup>. As indicated by tests, 10 volume percent of Schercomid SCO-EX<sup>①</sup> could disperse at least 20 volume percent of water, while 10 volume percent of Clindrol 101 CG<sup>①</sup> emulsified at least 15 volume percent of water.

Finally, in the fuel blends prepared for combustor testing in Phase II and III of the program, the surfactant with Schercomid SO-A<sup>①</sup> from Scher Chemical Company was selected for the preparation of the aqueous methanol and ethanol and the anhydrous methanol in JP-4 and JP-8 microemulsions. The JP-8 blends required a higher concentration of SO-A than the corresponding JP-4 blends. In preparing the water/fuel microemulsions, two surfactants, Clindrol 100 CG<sup>②</sup> and Clindrol 101 CG<sup>③</sup> from Clintwood Chemical Company were selected for the respective JP-4 and JP-8 blends. The pertinent properties of these surfactants are given below in Table 6.

TABLE 6. PHYSICAL AND CHEMICAL PROPERTIES OF SURFACTANTS

Gross	SO-A <sup>①</sup>	Clindrol 100 CG <sup>②</sup>	Clindrol 101 CG <sup>③</sup>
Heat of Combustion (Btu/lb)	15,680	14,025	14,405
Hydrogen, wt%	11.73	11.2	11.2
Carbon, wt%	71.49	58.9	59.3
Oxygen, wt%	12.99	25.53	25.13
Nitrogen, wt%	3.79	4.37	4.37
Specific Gravity	0.9539	0.9985	0.9896

Fuels containing the smoke suppressant ferrocene were prepared by dissolving the ferrocene in the base fuel followed by addition of surfactant and dispersed phase. Hydrazine in the form of hydrazine hydrate was added to an anhydrous ethanol/fuel blend because it had very limited solubility in the neat JP-4 and JP-8 base fuels. This method of increasing the solubility of hydrazine in petroleum-based fuels has been previously reported.(3)

A summary of all the fuel blends prepared for combustor testing is shown in Table 7.

#### Results of Preliminary Combustor Testing

In Phase II the fuel blends identified in Table 7 were tested at the takeoff operating condition to determine if significant reductions in exhaust smoke could be achieved; this operating condition was selected because it is the smokiest condition. A 40-percent reduction in smoke number was considered significant, since in the earlier Navy work(1,2), that percentage corresponded to a reduction in the J-79 plume visibility from Ringleman 2.5 to 1.

Figures 7(a), 7(b), and 7(c) show the effects of adding ethanol, methanol, and water, respectively, on the smoke number. All three gave significant reductions in smoke number with modest concentrations.

Figures 8(a) and 8(b) show the relative fuel cost to reduce exhaust smoke. The relative smoke number is plotted against the relative fuel cost in dollars/million Btu because it is the heat input rate required to maintain a specific combustor operating condition that is important. In comparing the slopes of the curves shown in Figures 8(a) and 8(b), it is apparent that the anhydrous ethanol solutions are most cost effective. It is clear that the aqueous methanol microemulsion costs the most whereas the other microemulsions made with anhydrous methanol, aqueous ethanol, and water are about the same.

TABLE 7. FULL MICROEMULSIONS AND SOLUTIONS TESTED

## Part 1. JP-4 Fuel

JP-4 (Vol%)	Ethanol (Vol%)	Methanol (Vol%)	Water (Vol%)	Clindrol <sup>®</sup> 100CG (Vol%)	SO-A <sup>®</sup> (Vol%)	Ferrocene (Wt%)	Hydrazine (Wt%)
* 90	10						
85 #	15						
* 80	20						
75 #	25						
60 #	40						
* 87	9.3		0.7		3		
* 77	18.6		1.4		3		
* 87		10			3		
* 77		20			3		
* 80		9.3	0.7		10		
* 60		18.6	1.4		20		
90 #			5	5			
* 80 #			10	10			
70 #			15	15			
* 60			20	20			
100 #						0.01	
85 #	15					0.01	
90 #			5	5		0.01	
**85	15						0.1
**84.5	15						0.6
**85	15					0.01	0.1
90 #				10			

## Part 2. JP-8 Fuel

JP-8 (Vol%)	Ethanol (Vol%)	Methanol (Vol%)	Water (Vol%)	Clindrol <sup>®</sup> 100CG (Vol%)	SO-A <sup>®</sup> (Vol%)	Ferrocene (Wt%)	Hydrazine (Wt%)
* 90	10						
85 #	15						
* 80	20						
75 #	25						
60 #	40						
* 85	9.3		0.7		5		
* 75	18.6		1.4		5		
* 84		10			6		
* 70		20			10		
* 79		9.3	0.7		11		
* 60		18.6	1.4		20		
90 #			5	5			
* 80 #			10	10			
70 #			15	15			
* 60			20	20			
100 #						0.01	
85 #	15					0.01	
90 #			5	5		0.01	
**85	15					0.01	0.1
90 #				10			

\* Fuel blends tested at the takeoff condition in Phase II

\*\* Tested only at the takeoff condition

# Tested at all operating conditions shown in Table 1

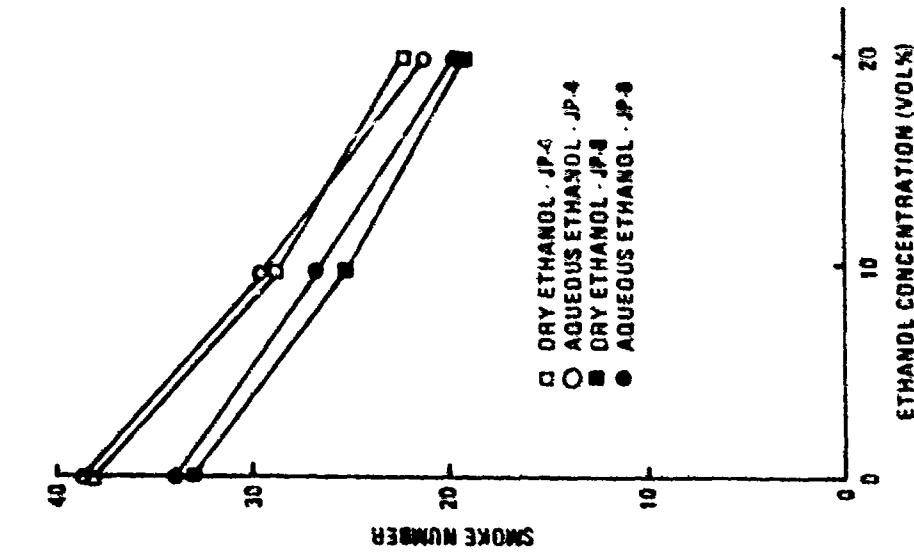


Figure 7(a). Effect of Ethanol Concentration on Exhaust Smoke Number

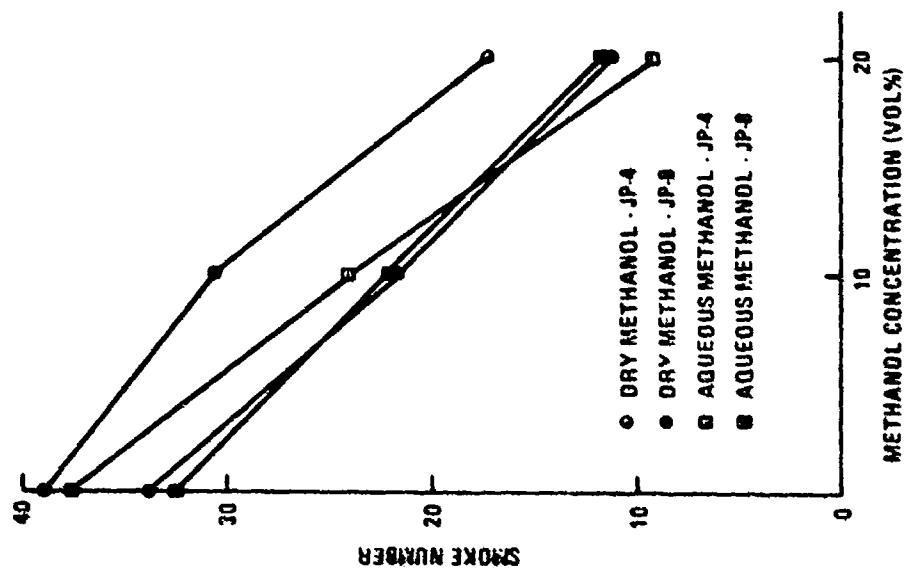


Figure 7(b). Effect of Methanol Concentration on Exhaust Smoke Number

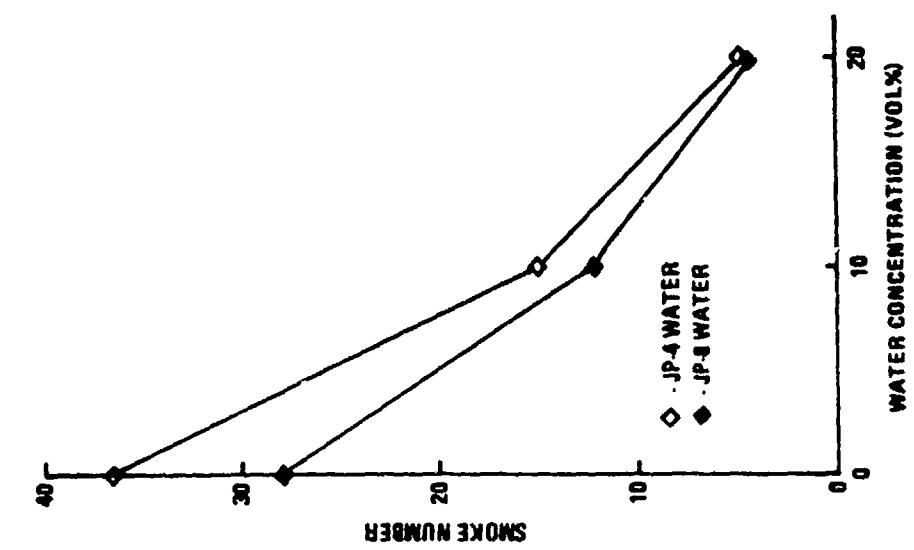


Figure 7(c). Effect of Water Concentration on Exhaust Smoke Number

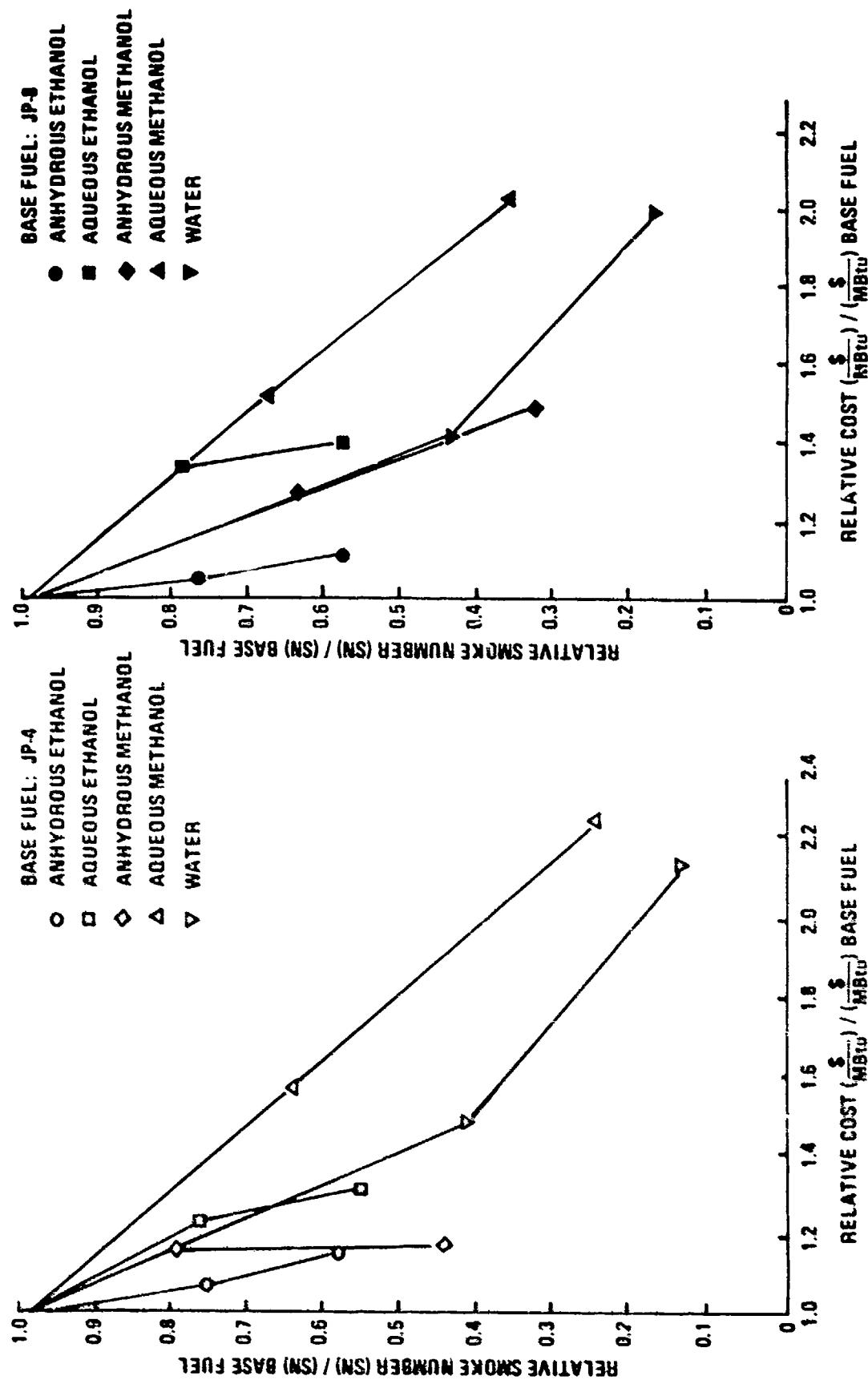


Figure 8 (a). Relative Cost to Reduce Smoke Number  
Base Fuel: JP-4

Figure 8 (b). Relative Cost to Reduce Smoke Number  
Base Fuel: JP-8

Figures 9(a) and 9(b) show the relative increase in fuel flow rate that is associated with the reduction in exhaust smoke number. This can be a significant factor in operating the engine because there are limits to the amount of fuel that can be delivered to the combustor by means of the fuel atomizing nozzle. Unfortunately, the results illustrated in Figures 9(a) and 9(b) are undiscerning; the methanol fuels show only a slight advantage over the ethanol fuels.

In considering both of the criteria given above, fuels blended with ethanol are favored most. Anhydrous ethanol solutions also have the advantage of being two component systems, which simplifies the blending of fuels for engine testing. The aqueous ethanol microemulsions require relatively low surfactant concentrations, especially at high ethanol concentrations.

It was therefore decided that continuation with the next phase of comprehensive testing was justified and that the testing should be done with the ethanol/fuel solution and water/fuel emulsion systems.

#### Comprehensive Combustion Performance Testing

The comprehensive testing was done at the four combustor operating conditions given in Table 1, ranging from idle to full power. The details of the fuel blends are given in Table 7.

The effects of water and ethanol concentrations in JP-4 and JP-8 on combustion performance were determined. This included the measurement of exhaust smoke number, flame radiation in the primary zone of the combustor, and the gaseous emissions (THC, CO and NO<sub>x</sub>); combustion efficiency was calculated. The test results in tabulated form are given in Appendix A. The effects of ethanol and water on exhaust smoke and flame radiation are shown in Figures 10 through 13; the effects on the gaseous emissions and combustion efficiency are shown in Figures 14 through 17. In general, exhaust smoke and flame radiation were reduced by all the emulsions while carbon monoxide and total hydrocarbon emissions increased, thus reducing combustion efficiency.

Water and ethanol were both very effective in reducing soot formation. It will be shown later that their effectiveness is determined by the degree with which they increase the hydrogen/carbon ratio of the fuel blend. At the highest power (takeoff) condition, water and ethanol gave the most significant reductions in exhaust smoke and flame radiation while the changes in the emissions of total hydrocarbons and carbon monoxide were very modest. As the power was reduced, the effect of water and alcohol on smoke and radiation became less dramatic but the emissions of hydrocarbons and carbon monoxide increased. The total hydrocarbon and carbon monoxide emissions were considerably higher in the case of the water/fuel microemulsions than the ethanol/fuel solutions. In earlier work with water/fuel macroemulsions, it was also found that the emissions of hydrocarbons and carbon monoxide were increased dramatically at the ground idle operating conditions. In fuel blends containing only the surfactant (Clindrol 100 CG<sup>®</sup>), the hydrocarbon and carbon monoxide emissions were about the same as the neat fuel, indicating these higher boiling point materials were not the cause. The effect would therefore appear to be differences in fuel atomization and vaporization rates because, at low power conditions, combustion is controlled largely by the fuel vaporization process.

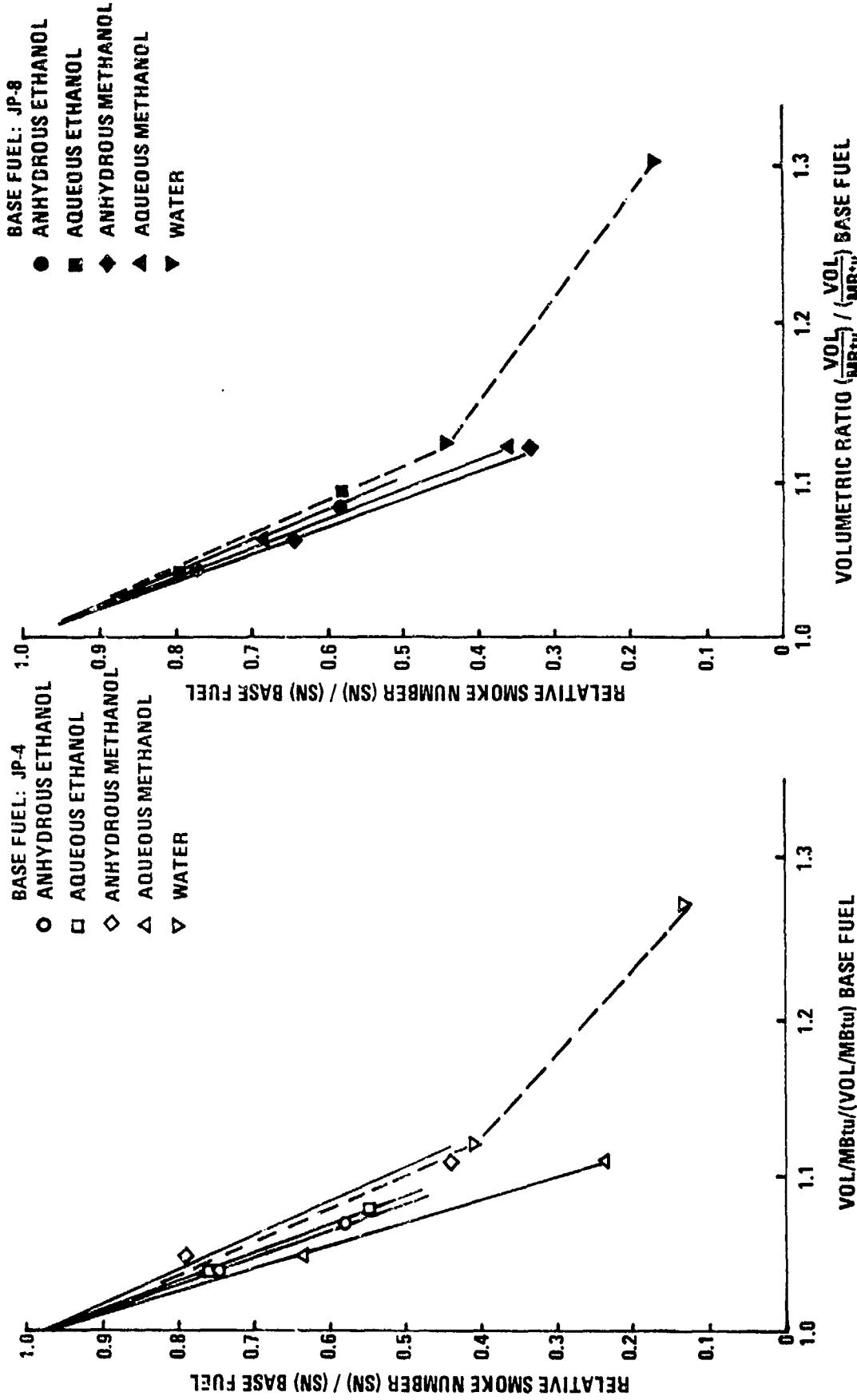


Figure 9(a). Increase in Fuel Flow Rate Associated With Reductions in Smoke Number, Base Fuel JP-4

Figure 9(b). Increase in Fuel Flow Rate Associated With Reductions in Smoke Number, Base Fuel JP-8

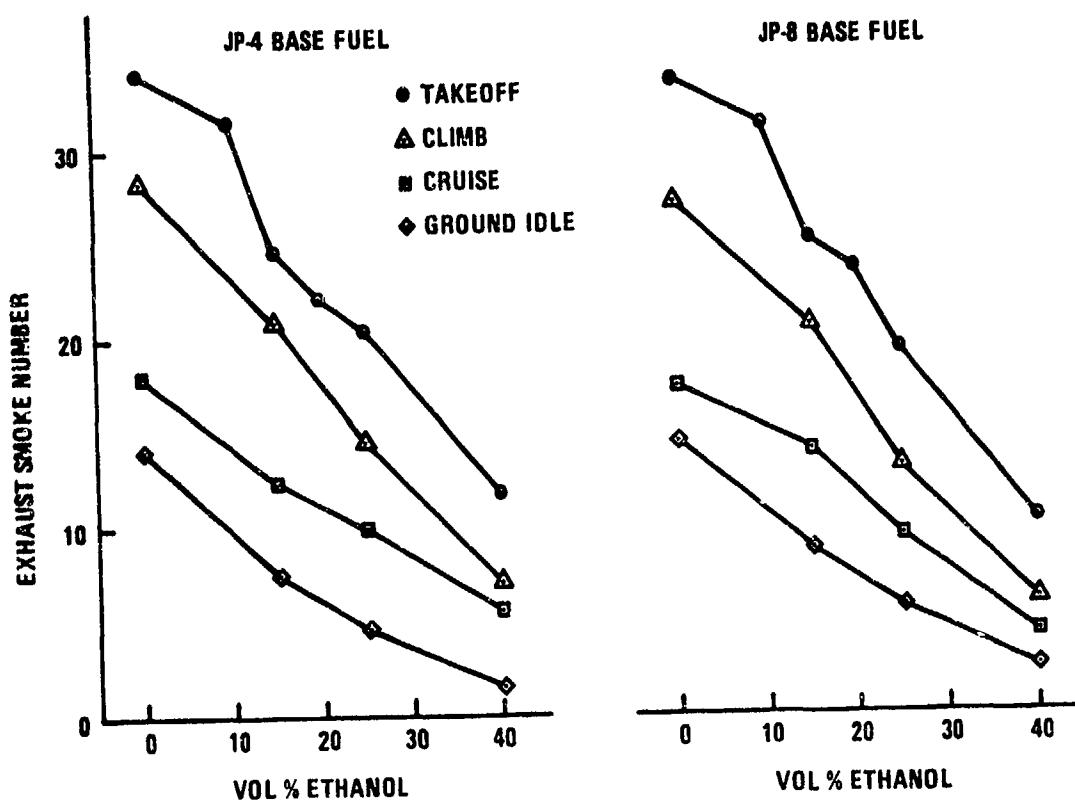


Figure 10. Effect of Ethanol Concentration on Exhaust Smoke

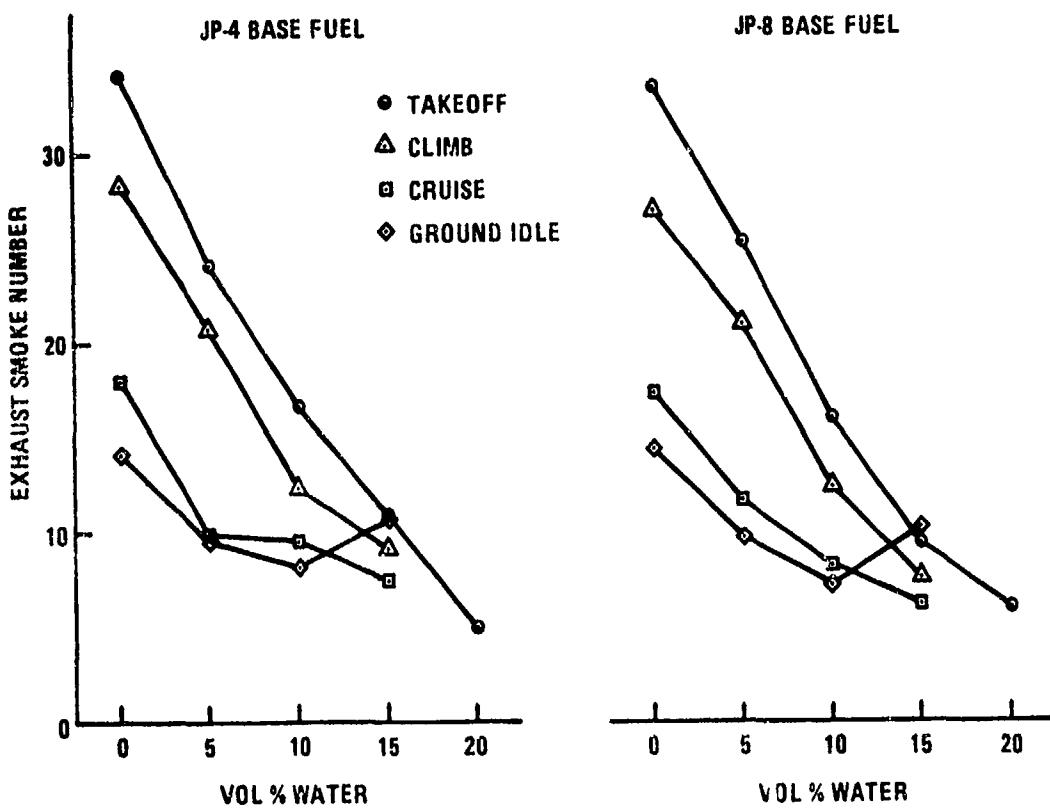


Figure 11. Effect of Water Concentration on Exhaust Smoke

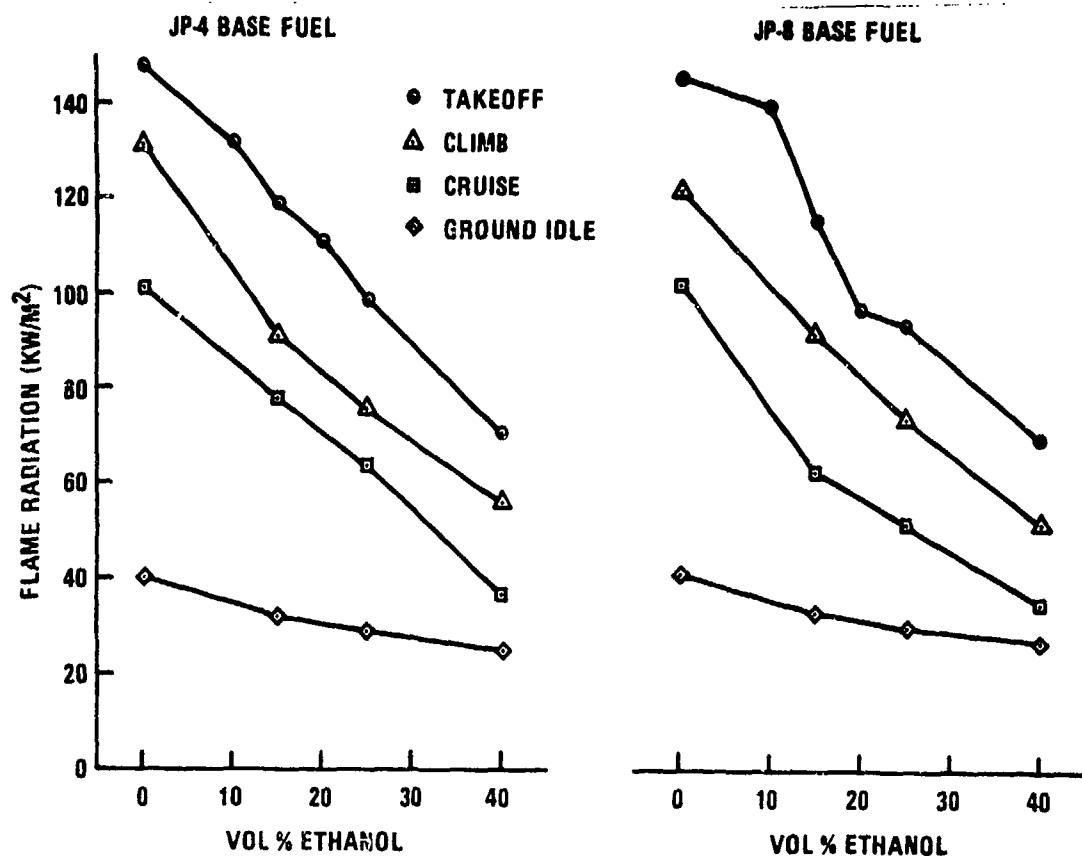


Figure 12. Effect of Ethanol Concentration on Flame Radiation

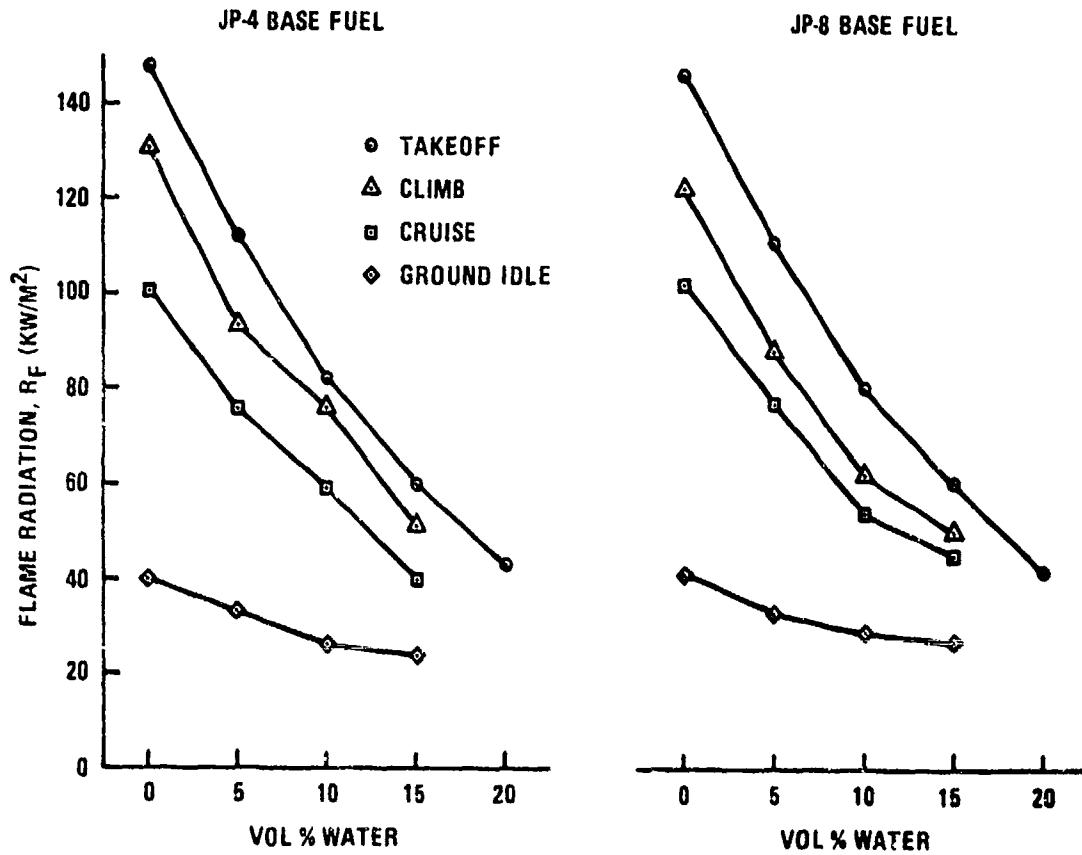


Figure 13. Effect of Water Concentration on Flame Radiation

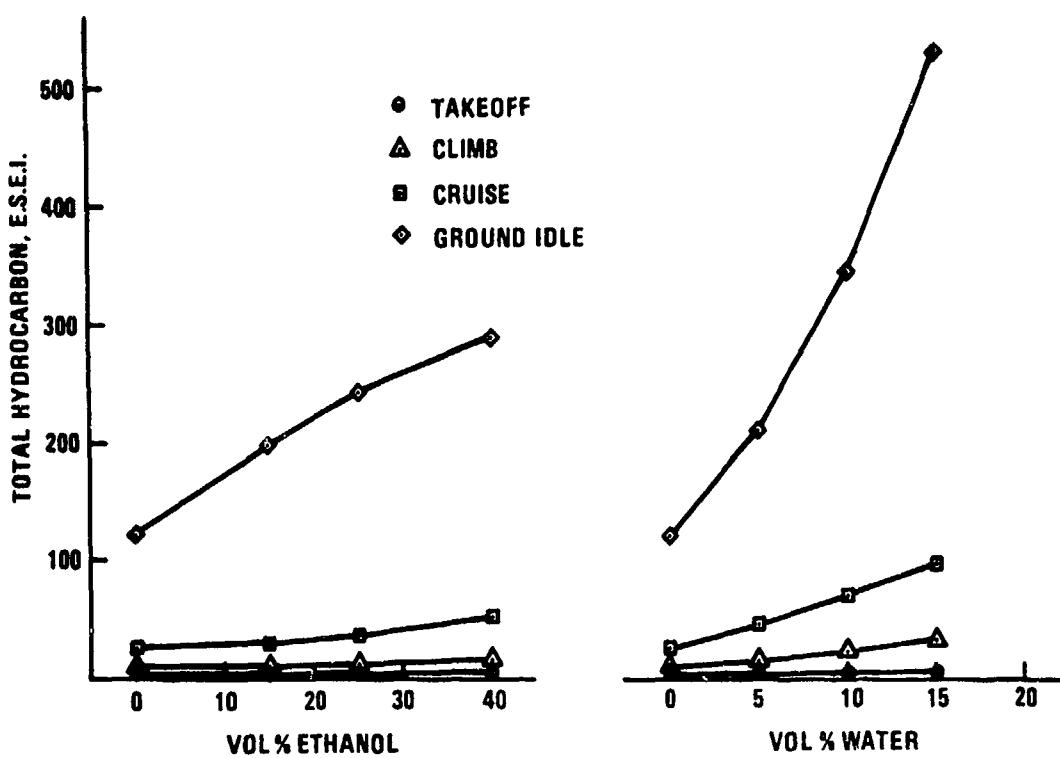


Figure 14. Effects of Ethanol and Water on Exhaust Hydrocarbons: JP-8 (Energy Specific Emissions Index)

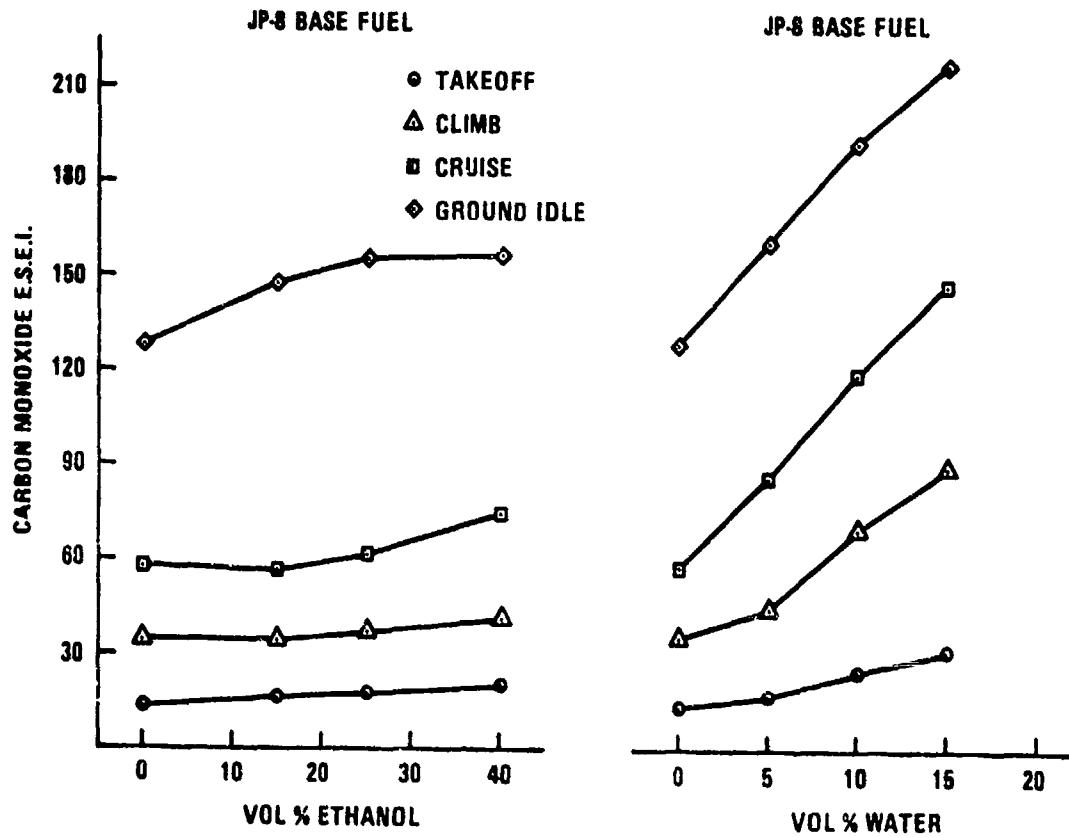


Figure 15. Effects of Ethanol and Water on Carbon Monoxide: JP-8 (Energy Specific Emissions Index)

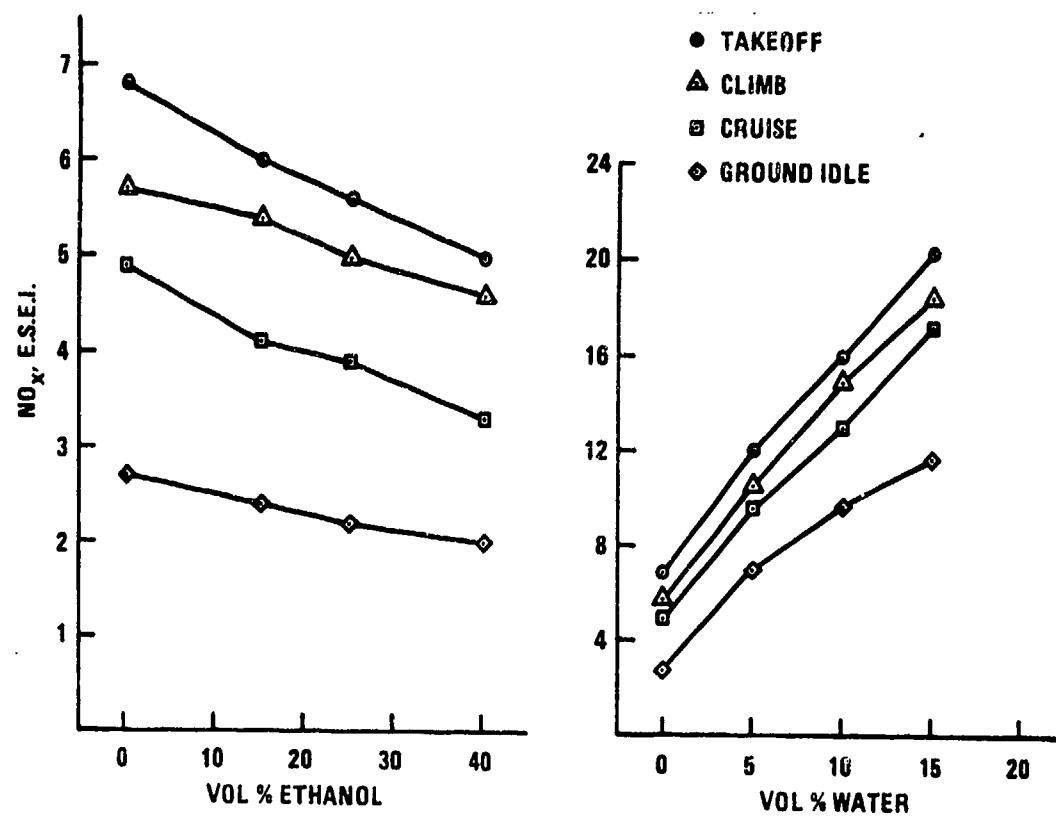


Figure 16. Effect of Ethanol and Water on Exhaust  $\text{NO}_x$ : JP-8 (Energy Specific Emissions Index)

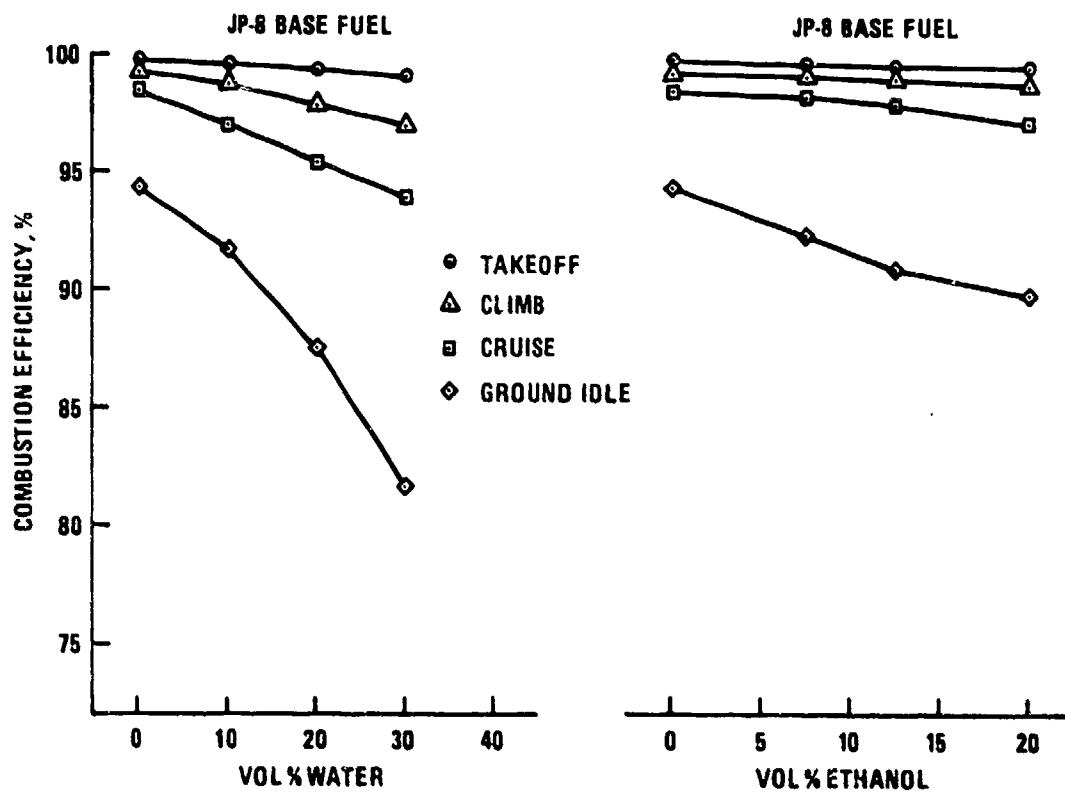


Figure 17. Effect of Ethanol and Water on Combustion Efficiency: JP-8

The fuel properties that affect atomization and droplet vaporization are viscosity and boiling point distribution, respectively. The viscosity of the water/fuel microemulsion was much higher than that of the ethanol/fuel blend. This would result in a significant difference in the Sa <sub>ter</sub> mean diameter of the fuel droplets in the sprays and a corresponding difference in the rates of vaporization. It is well known that the fuel droplet vaporization time is proportional to the square of the droplet diameter(7).

The effect of boiling point distribution is speculative because of the complex nature of the vaporization process for immiscible systems (emulsions) and non-ideal solutions such as alcohol/fuel blends. The temperature of a vaporizing droplet is approximately equal to the boiling point of the most volatile component in the fuel; for JP-8, there is little doubt that water and ethanol are the lowest boiling point components. In JP-4 there are some hydrocarbons in the same boiling point range as ethanol and water, but they are probably in relatively low concentration. Thus, in either case of JP-4 or JP-8, the rate of vaporization of a droplet containing ethanol would be slower than that of the neat fuel droplet because the temperature of the droplet would be depressed by the presence of ethanol. This may account for the increased total hydrocarbons and carbon monoxide that are formed by the ethanol/fuel blends. It appears that this effect would be greater for water even though its boiling point is higher than that of ethanol. Ethanol is able to burn and thereby transfer heat back to the droplet whereas the vaporization of the water-containing droplet is more dependent on convective heat transfer from the surrounding gas. Because of the immiscible nature of the water/fuel emulsion, the water evaporates much more freely; this suggests the possibility that the fuel droplet may not ignite until most of the water has evaporated. The water with its relatively high enthalpy of vaporization evaporates preferentially and suppresses the volatilization of combustible components. This cooling effect, combined with the relatively high viscosity of the water/fuel microemulsions, may account for the substantial increase in hydrocarbon and carbon monoxide emissions that are observed.

It was found that while the ethanol blends reduced the oxides of nitrogen, the water-in-fuel microemulsions increased them significantly because the surfactant contained nitrogen. It was not possible to calculate the conversion of fuel-bound nitrogen to NO <sub>x</sub> relative to that produced by the Zeldovich mechanism (thermal NO <sub>x</sub>)(7), because the effect of water was not known. In the earlier work with macroemulsified fuels where the surfactant was free of nitrogen, the NO <sub>x</sub> was reduced significantly by the presence of water and undoubtedly would <sup>x</sup>have been here also.

Fuel blends of JP-4 and JP-8 containing 10-percent surfactant were tested at all four operating conditions. In these experiments, it was possible to determine the conversion of fuel-bound nitrogen to NO <sub>x</sub> by simply comparing the NO <sub>x</sub> produced by the surfactant-containing fuel with that of the neat fuel. It was found that the conversion efficiencies (78 and 63 percent for JP-4 and JP-8, respectively) were essentially the same at all operating conditions. These fuel blends contained 0.437 percent nitrogen; according to Blazowski(8), the percent conversion to NO <sub>x</sub> is inversely proportional to the concentration of fuel-bound nitrogen.

### Smoke Suppressant Additives

The metallic smoke-suppressant additive, ferrocene, was examined for possible synergisms with the water and ethanol in JP-4 and JP-8 fuel blends. Ferrocene, dicyclopentadienyl iron, is a solid organo-metallic compound that is sparingly soluble in hydrocarbons. When used as a smoke-abatement fuel additive in test cell applications, the concentration is quite low, generally less than 0.05 percent, so it is first dissolved in xylene to simplify the metering of such small amounts of additive into the fuel stream. In the present work, the ferrocene was dissolved in the JP-4 and JP-8 base fuels before the water, ethanol, and surfactant were added.

Early studies by Friswell(9) and Shirmer(10) and recent work by the USAF(11) have shown that ferrocene and a similar organometallic of manganese give significant reductions in exhaust smoke from gas turbines but have virtually no effect on primary zone flame radiation and liner temperature. This is confirmed by the result shown in Figure 18 where the exhaust smoke is reduced,

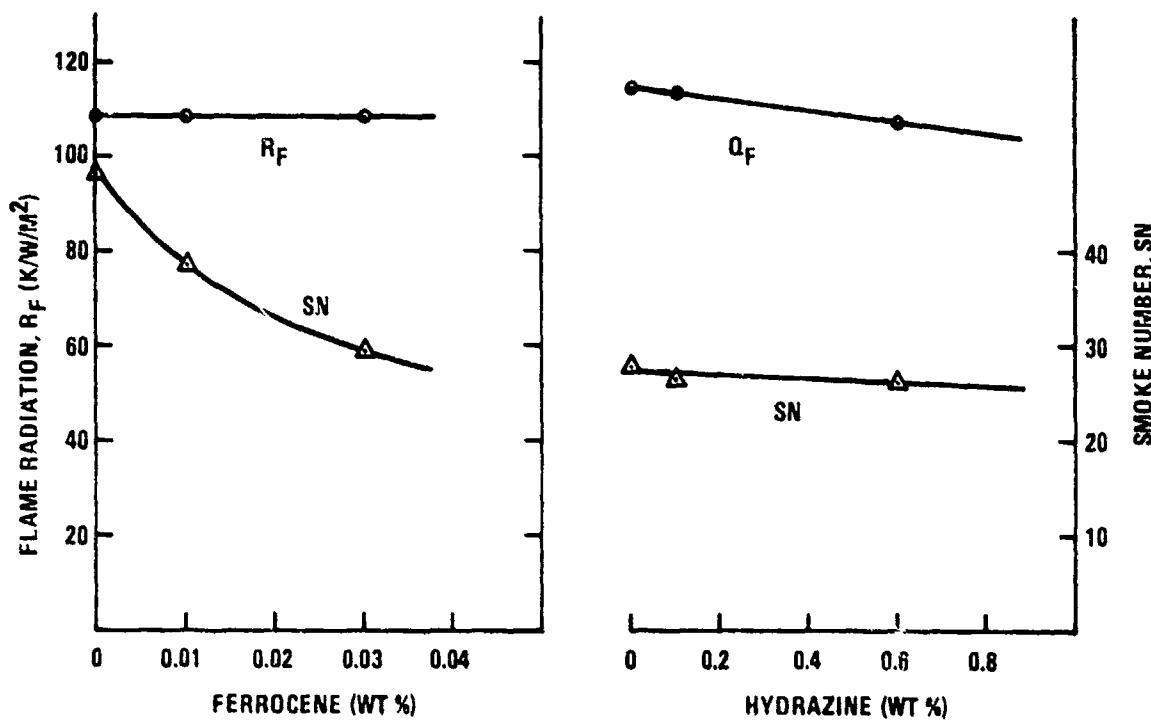


Figure 18. Effect of Ferrocene and Hydrazine on Flame Radiation and Exhaust Smoke

but the flame radiation is unchanged by the presence of ferrocene in a Jet A reference fuel. Cotton, Friswell, and Jenkins(12) suggest that the metal oxide is trapped within the soot particles and acts as an oxidation catalyst. In oxygen-rich flames, it appears that the metal is readily oxidized, forming a superoxide  $MO_2$ , which acts as an intermediate that reduces the activation energy of the carbon-oxygen reaction.

Figure 19 compares the effect on exhaust smoke when ferrocene is added to the neat fuel, water/fuel microemulsions, ethanol/fuel solutions, and the reference fuel Jet A. The results show a similar smoke number reduction in all

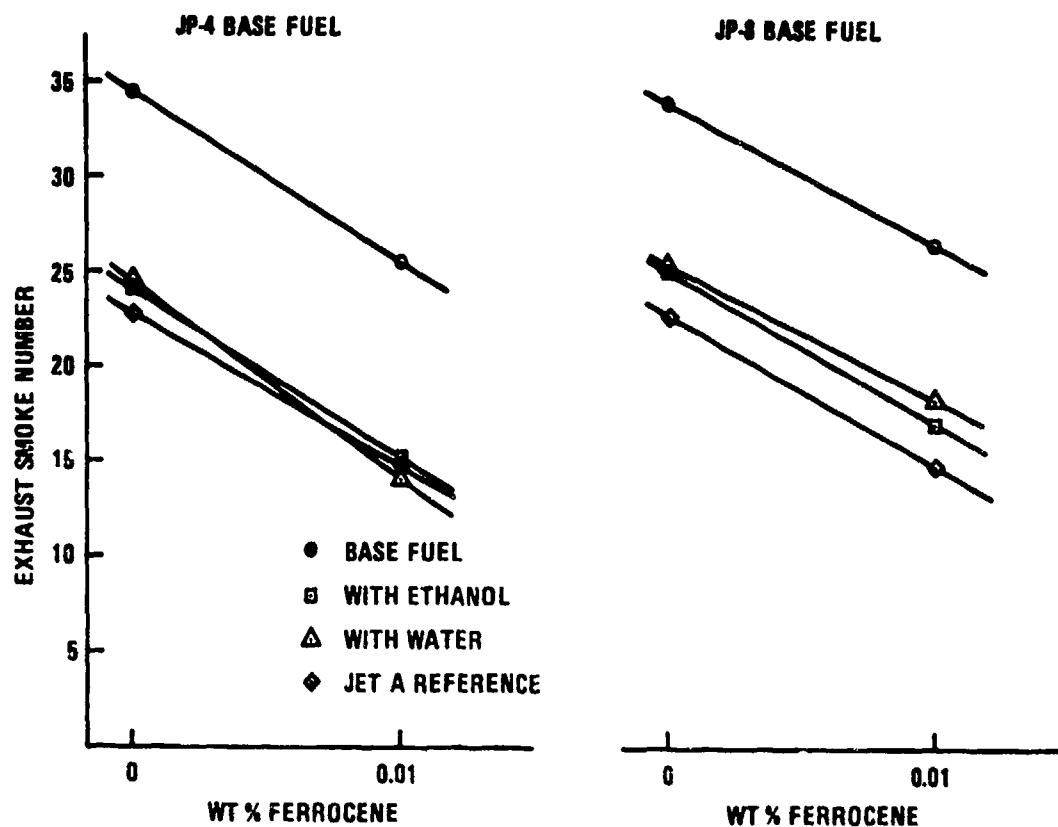


Figure 19. Synergistic Effects Between Microemulsions and Ferrocene

cases, indicating that there are no synergistic effects between ferrocene and the fuel blends. Perhaps iron in the form of a water-soluble inorganic salt such as  $\text{Fe}(\text{NO}_3)_3$  could be blended with the water/fuel microemulsions with the same effectiveness as ferrocene since the water in the test fuel did not have a deleterious effect on the performance of ferrocene. If the iron was in the water prior to fuel blending, this may be a more feasible approach from a system-operation standpoint.

Hydrazine was considered as a possible smoke suppressant additive for gas turbine use because it has been claimed that it can reduce smoke from utility-type burners(3). Figure 15 shows the effect of hydrazine on exhaust smoke and flame radiation. Hydrazine used in low concentrations (less than 0.1 percent) could reduce smoke dramatically by some unknown mechanism, or it could be used in higher concentrations (greater than 1 percent) to reduce smoke by increasing the hydrogen/carbon ratio of the fuel. Based on the results in Figure 18, the modest reductions in radiation and smoke can only be attributed to the H/C ratio effect. Since this addition is not effective except by in-

creasing the H/C ratio, there was no reason to expect any synergistic effects with the emulsions, and no further work was done with hydrazine.

#### Deposits

Ferrocene is known to produce iron-oxide deposits on engine parts such as the combustor liner and the turbine blades. Tests were conducted to compare the deposits formed by water and ethanol/fuel/ferrocene blends with those of neat fuel/ferrocene blends. The fuels were each run for twenty-five minutes at each of the four operating conditions given in Table 1. The burner-can was weighed and photographed after each test. The photographs comparing the condition of the burner-can and turbine-inlet-annulus after exposure to various test fuels are shown in Figure 20. The orange deposit (iron oxide) appears to be about the same for the neat fuel and ethanol fuel blends containing ferrocene. The water/fuel microemulsion containing ferrocene exhibited a yellowish-type deposit that seemed to consist of iron oxide and a varnish which may have been formed from the surfactant.

The changes in weight of the burner-can are given in Table 8.

TABLE 8. DEPOSIT FORMATION/WEIGHT CHANGE OF BURNER CAN

<u>Fuel With 0.01% Ferrocene</u>	<u>Weight Change, g</u>
Neat JP-4	0.1
Neat JP-8	0.17
Ethanol/JP-4	0.22
Ethanol/JP-8	0.20
Water/JP-4	2.52
Water/JP-8	0.55
JP-4/Clindrol 100 CG <sup>①</sup> without Ferrocene	0.5
JP-8/Clindrol 101 CG <sup>①</sup> without Ferrocene	0.5
JP-4 and JP-8 without Ferrocene	no change

The results indicate that deposits with ethanol/fuel blends are slightly higher than with the neat fuels; deposits with the water/fuel microemulsions are obscured by varnish-type deposits that probably come from the surfactant.

Note that the deposits with the water/fuel microemulsions were of the same order as the JP-4/Clindrol 100 CG<sup>①</sup> and JP-8/Clindrol 101 CG<sup>①</sup> blends not containing ferrocene.

#### Cost Effectiveness

Figure 21 shows the relative cost to reduce the smoke number of the base fuel by adding water and alcohols. The anhydrous ethanol solutions appear to be the most effective from a cost standpoint. However, the water-in-fuel microemulsions are quite effective considering the high surfactant concentration and its high cost (\$0.80/lb) compared with anhydrous ethanol (\$0.30/lb). Actually, ferrocene turns out to be most cost effective when compared with the water/fuel and alcohol/fuel blends tested in this program. The reduction in smoke (about 10 smoke numbers) achieved by adding 0.01 percent ferrocene to the neat fuel is approximately the same as adding 5-percent water or 15-per-

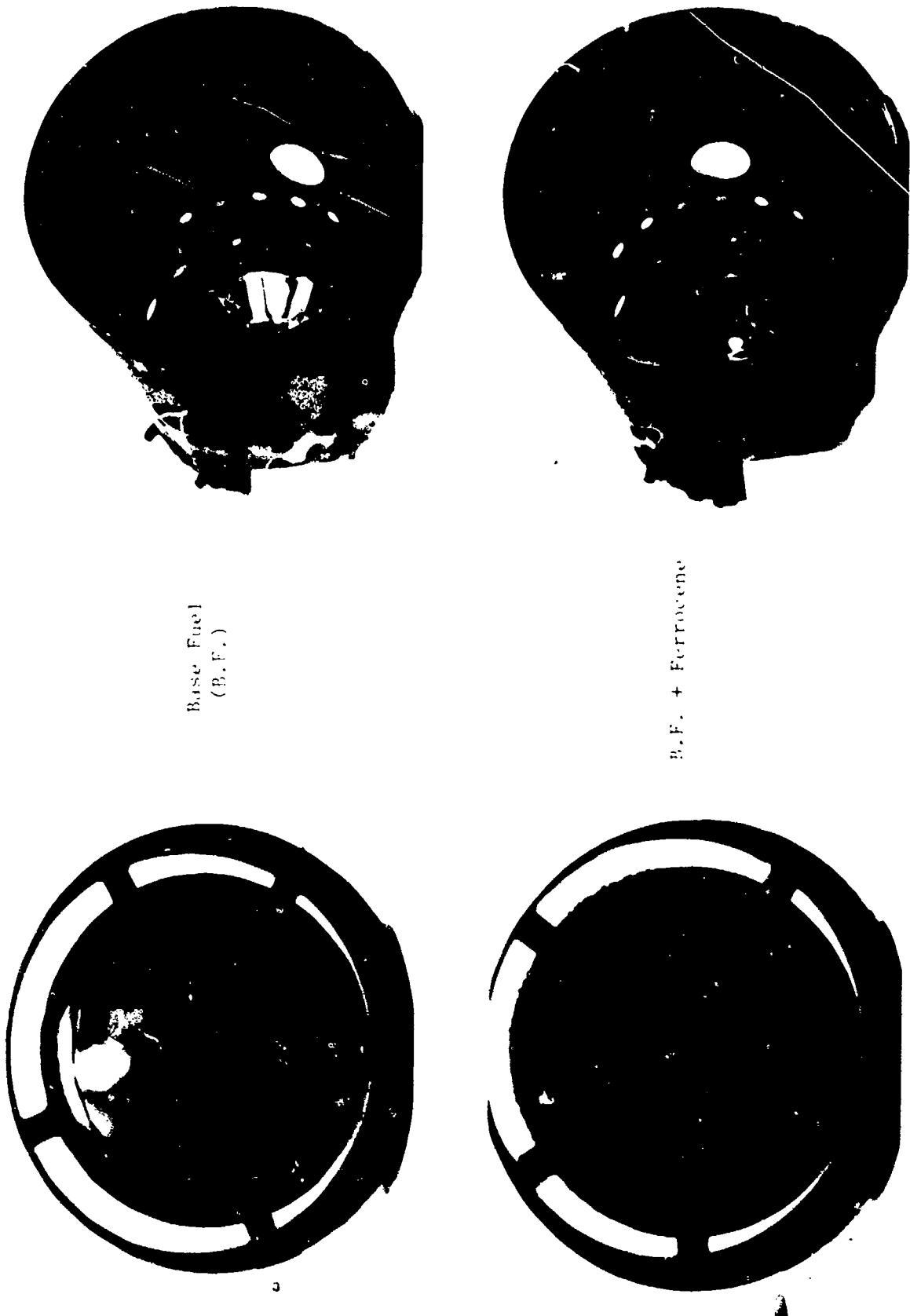


Figure 20. Synergistic Effects on Ferrocene Deposits



R.F. + Ferrocene  
+ 15% Ethanol



R.F. + Ferrocene  
+ 5% Water

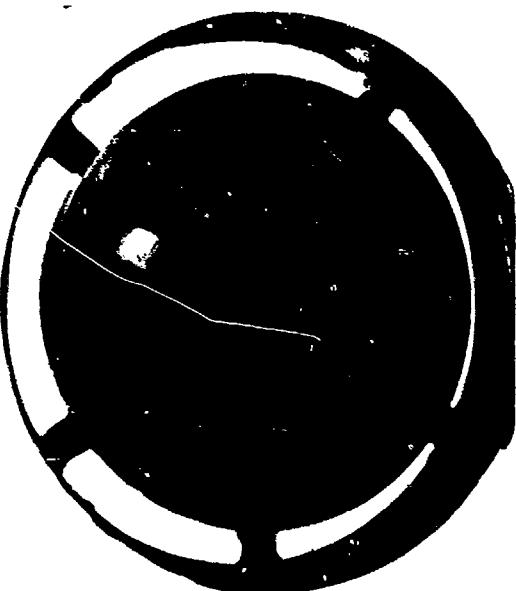


Figure 20. Schematic Effects on Ferrocene Deposits (Concluded)

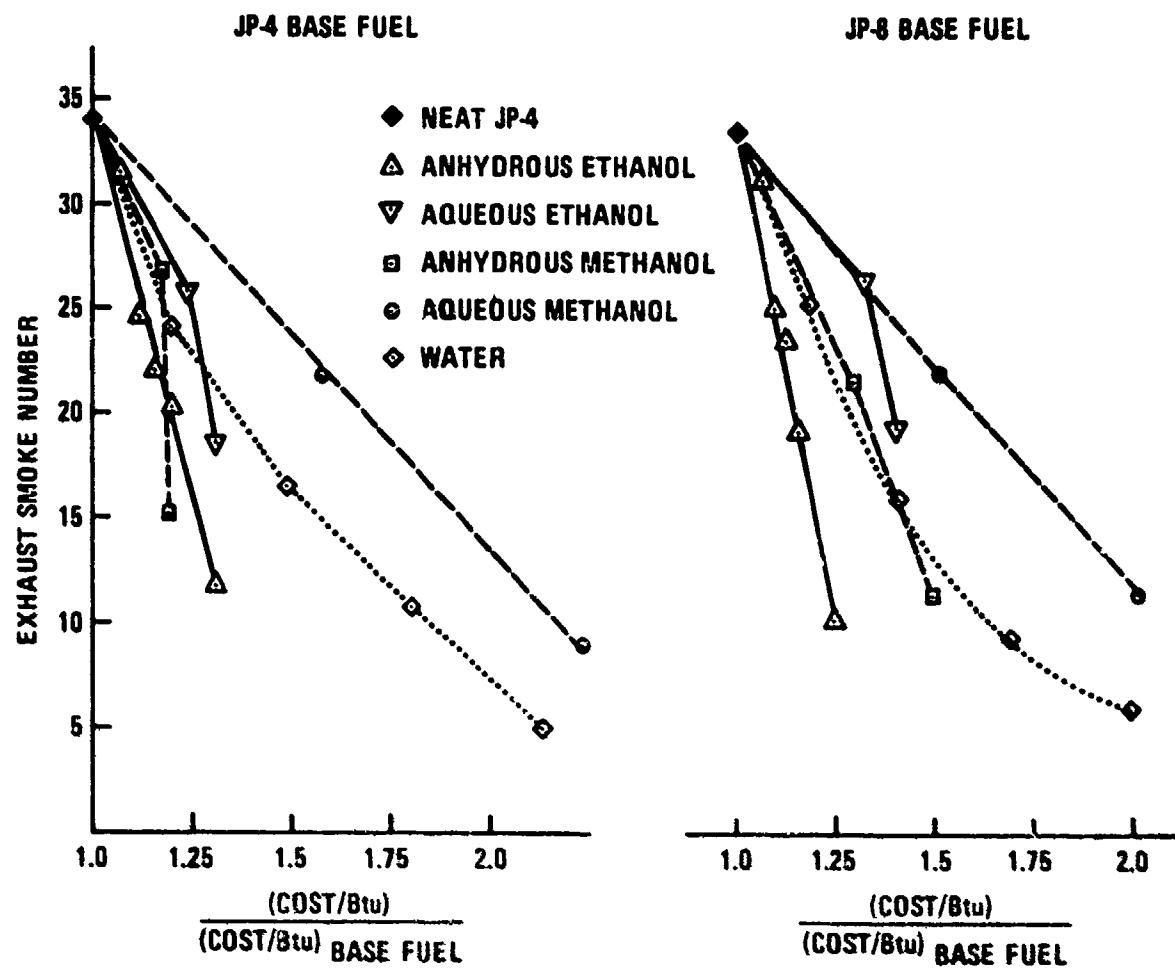


Figure 21. Relative Cost to Reduce Exhaust Smoke: Takeoff Condition

cent ethanol. The increase in cost of a fuel containing 0.01-percent ferrocene (bulk cost approximately 2 cents/gram) is about 0.6 cents/gallon and that of the water and ethanol blends is of the order of 20 cents/gallon. However, the low cost of ferrocene itself may be overshadowed by the added cost of maintenance resulting from deposition and corrosion.

#### Flow Rate Penalty

When a component such as water is blended with fuel, the energy density of the fuel is reduced so that it is necessary to increase the fuel flow rate to the engine in order to sustain the same power output. Figure 22 shows the increase in fuel flow rate associated with reductions in smoke. From an energy density standpoint alone, alcohols reduce this penalty because they have a heat of combustion although less than that of jet fuel. However, somewhat surprisingly, the results indicate that the smoke reduction is accompanied by about the same flow rate penalty for all the fuel blends.

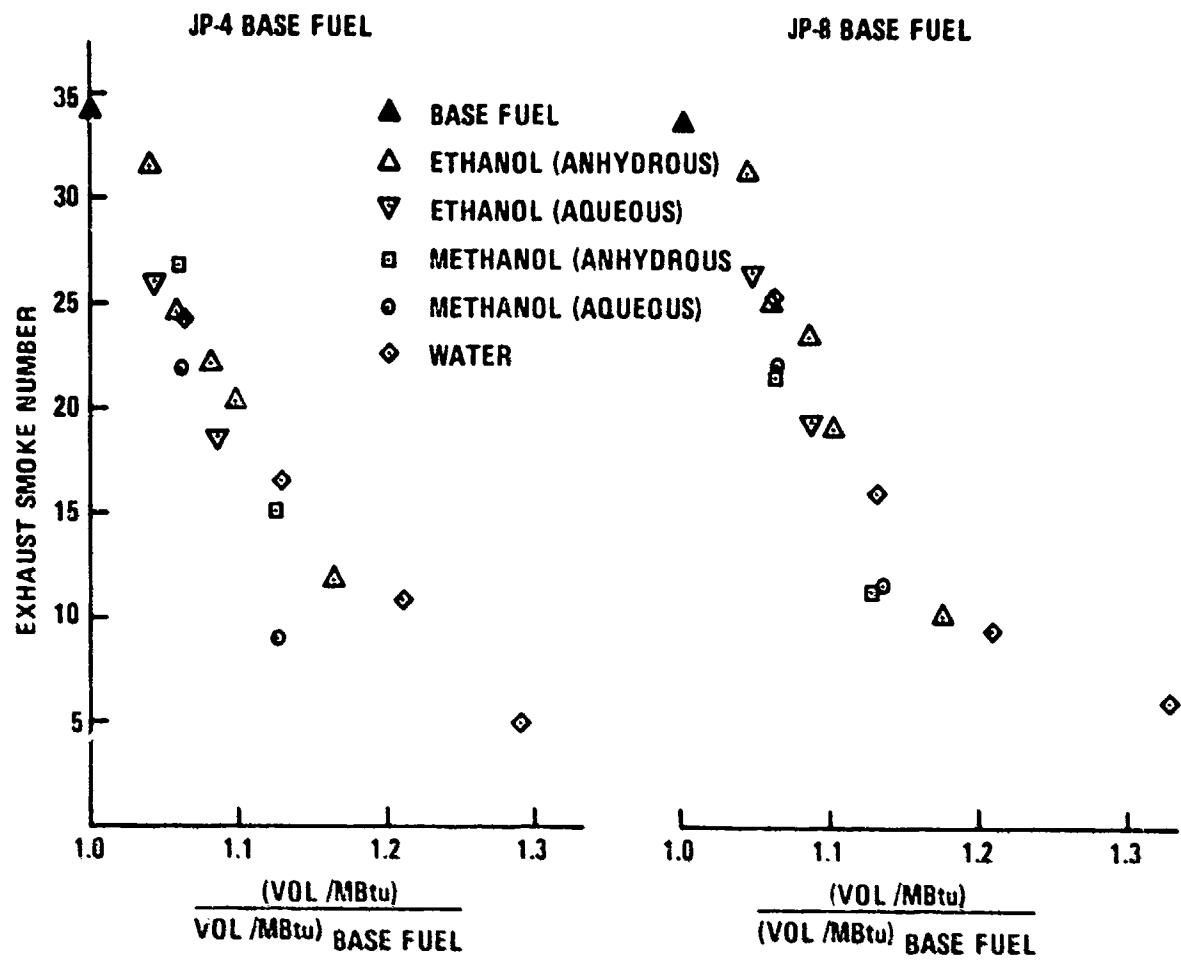


Figure 22. Increase in Fuel Flow Rate Associated With Reductions in Exhaust Smoke: Takeoff Condition

#### Hydrogen/Carbon Ratio

Several studies(13-16) have shown that hydrogen/carbon ratio is a good correlating parameter for soot formation in gas turbine engines. Recent work(17) by the contractor has shown that this correlation can be extended to hydrocarbon fuels containing oxygenates and dispersed water. The correlations of smoke number and radiation with H/C atom ratio in Figure 23 include two sets of data; the open symbols are an earlier study which included six JP-5 petroleum fuels, three JP-5 fuels derived from coal, oil shale and tar sands, seven fuels blended from JP-5 and diesel marine, six water-in-fuel macroemulsions and two methanol-in-fuel (high aromatic fuel) solutions, and the closed symbols represent this work. It is apparent that the microemulsions and ethanol solutions correlate with H/C atom ratio in the same way as the other fuels.

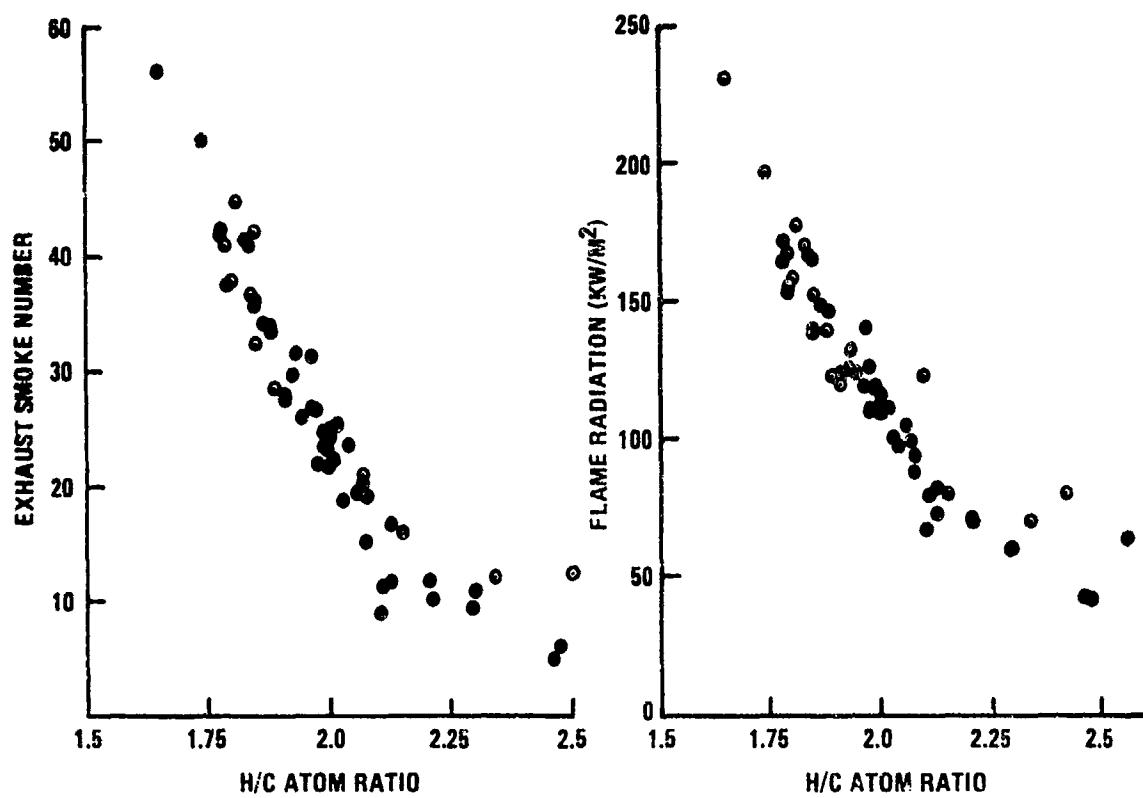


Figure 23. Correlation of Exhaust Smoke and Flame Radiation With Hydrogen/Carbon Ratio

## SECTION IV

### CONCLUSIONS

1. Microemulsions of water, methanol, and ethanol (aqueous) in JP-4 and JP-8 can be formulated.
2. Ethanol (anhydrous) is soluble in JP-4 and JP-8.
3. These blends affected combustor performance as follows:
  - Reduce soot formation.
  - Reduce exhaust smoke.
  - Reduce oxides of nitrogen\*.
  - Increase CO.
  - Increase total hydrocarbons.
  - Decrease combustion efficiency.
4. The last three detrimental effects are only important at low-power operating conditions such as ground idle where smoke is low and the additives are not required.
5. Addition of ferrocene reduced exhaust smoke but not flame radiation (soot production) and therefore acts as an oxidation catalyst on the soot.
6. No synergistic effects were found on concentration effectiveness.
7. Deposits with ethanol/fuel blends were slightly higher but may have been within experimental error; deposits with water/fuel blends were obscured by other deposits.
8. Hydrazine had no apparent effect on soot/smoke other than that generated by its hydrogen content.
9. Smoke and radiation reductions from the addition of water and alcohol correlated with changes in hydrogen/carbon ratio.
10. Ethanol (dry) solutions appear to be the most effective from the standpoint of cost, operational, and system effects. Metal additives cost less, but present other problems.

\* Increased  $NO_x$  when surfactant contained nitrogen.

## SECTION V

### RECOMMENDATIONS

1. Full-scale engine tests on the ethanol/fuel blends should be conducted.
2. The opportunities for using water or alcohol as a carrier (solute) for smoke-suppressant additives should be evaluated. Inorganic salts cost less and could be stored in the water and possibly the ethanol.
3. The role of metal additives in soot formation and oxidation should be studied. The mechanisms for heterogeneous and gas phase catalytic effects and the importance of ions in the nucleation process are still in a very speculative stage.
4. The effects of fuel molecular structure on soot formation should be studied to provide a better understanding of the kinetic processes involved.

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APPENDIX A

FLAME RADIATION, R, AND EXHAUST SMOKE NUMBERS, SN,  
FOR THE TEST FUELS AT THE SELECTED OPERATING CONDITIONS

Table A-1 contains flame radiation and exhaust smoke numbers  
for the test fuels at selected operating conditions.

TABLE A-1. FLAME RADIATION (R) AND EXHAUST

Fuel Description	Takeoff		Climb		Cruise	
	R(kW/M <sup>2</sup> )	SN	R(kW/M <sup>2</sup> )	SN	R(kW/M <sup>2</sup> )	SN
Jet A Reference	109	21.8	89	15.3	71	12
JP-4 Base Fuel	148	34.1	131	28.3	101	18
JP-4 + 10% EtOH	132	31.5	---	---	---	---
JP-4 + 15% EtOH	119	24.6	91	20.9	78	12
JP-4 + 20% EtOH	111	22.1	---	---	---	---
JP-4 + 25% EtOH	99	20.3	76	14.5	64	9
JP-4 + 40% EtOH	71	11.8	56	7.0	37	5
JP-4 + 10% Aqueous EtOH + 3% SO-A <sup>①</sup>	124	26.0	---	---	---	---
JP-4 + 20% Aqueous EtOH + 3% SO-A <sup>①</sup>	100	18.7	---	---	---	---
JP-4 + 10% MeOH + 3% SO-A <sup>①</sup>	119	26.8	---	---	---	---
JP-4 + 20% MeOH + 3% SO-A <sup>①</sup>	88	15.1	---	---	---	---
JP-4 + 10% Aqueous MeOH + 10% SO-A <sup>①</sup>	110	21.8	---	---	---	---
JP-4 + 20% Aqueous MeOH + 20% SO-A <sup>①</sup>	67	9.0	---	---	---	---
JP-4 + 10% Clindrol 100 CG <sup>①</sup>	125	27.8	111	20.8	82	10
JP-4 + 5% H <sub>2</sub> O + 5% Clindrol 100CG <sup>①</sup>	112	24.2	93	20.1	76	9
JP-4 + 10% H <sub>2</sub> O + 10% Clindrol 100 CG <sup>①</sup>	82	16.6	76	12.4	59	9
JP-4 + 15% H <sub>2</sub> O + 15% Clindrol 100 CG <sup>①</sup>	60	10.9	51	9.2	40	7
JP-4 + 20% H <sub>2</sub> O + 20% Clindrol 100CG <sup>①</sup>	43	5.0	---	---	---	---
Jet A + 0.01% Ferrocene	109	14.8	---	---	---	---
Jet A + 0.03% Ferrocene	109	11.5	---	---	---	---
JP-4 + 0.01% Ferrocene	148	25.6	133	23.8	107	23
JP-4 + 15% EtOH + 0.01% Ferrocene	120	16.2	93	15.4	74	12
JP-4 + 5% H <sub>2</sub> O + 5% Clindrol 100 CG <sup>①</sup> + 0.01% Ferrocene	111	15.1	113	13.4	86	11
JP-4 + 15% EtOH + 0.1% Hydrazine	118	23.3	---	---	---	---
JP-4 + 15% EtOH + 0.6% Hydrazine	111	23.2	---	---	---	---
JP-4 + 15% EtOH + 0.01% Ferrocene + 0.1% Hydrazine	119	16.6	---	---	---	---
JP-8 Base Fuel	146	33.5	122	27.0	102	17
JP-8 + 10% EtOH	140	31.2	---	---	---	---
JP-8 + 15% EtOH	116	25.0	92	20.5	63	13
JP-8 + 20% EtOH	97	23.5	---	---	---	---
JP-8 + 25% EtOH	94	19.1	74	13.0	52	9
JP-8 + 40% EtOH	70	10.1	52	5.9	35	4
JP-8 + 10% Aqueous EtOH + 5% SO-A <sup>①</sup>	126	26.6	---	---	---	---
JP-8 + 20% Aqueous EtOH + 5% SO-A <sup>①</sup>	105	19.5	---	---	---	---
JP-8 + 10% MeOH + 6% SO-A <sup>①</sup>	110	21.6	---	---	---	---
JP-8 + 20% MeOH + 10% SO-A <sup>①</sup>	79	11.3	---	---	---	---
JP-8 + 10% Aqueous MeOH + 11% SO-A <sup>①</sup>	110	22.1	---	---	---	---
JP-8 + 20% Aqueous MeOH + 20% SO-A <sup>①</sup>	73	11.6	---	---	---	---
JP-8 + 10% Clindrol 101 CG <sup>①</sup>	125	29.6	109	24.9	83	13
JP-8 + 5% H <sub>2</sub> O + 5% Clindrol 101 CG <sup>①</sup>	111	25.3	88	21.0	77	11
JP-8 + 10% H <sub>2</sub> O + 10% Clindrol 101 CG <sup>①</sup>	80	16.0	62	12.4	54	8
JP-8 + 15% H <sub>2</sub> O + 15% Clindrol 101 CG <sup>①</sup>	60	9.4	50	7.5	45	6
JP-8 + 20% H <sub>2</sub> O + 20% Clindrol 101 CG <sup>①</sup>	42	6.0	---	---	---	---
JP-8 + 0.01% Ferrocene	146	26.6	122	22.3	92	13
JP-8 + 15% EtOH + 0.01% Ferrocene	116	17.0	81	13.5	64	12
JP-8 + 5% H <sub>2</sub> O + 5% Clindrol 101 CG <sup>①</sup> + 0.01% Ferrocene	110	18.4	89	6.4	70	10
JP-8 + 15% EtOH + 0.01% Ferrocene + 0.1% Hydrazine	121	15.9	---	---	---	---

(The reverse of

AND EXHAUST SMOKE NUMBERS (SN)

Cruise (kW/m <sup>2</sup> )	SN	Ground Idle	
		R(kW/m <sup>2</sup> )	SN
11	12.3	31	6.6
11	18	40	14.1
11	---	---	---
18	12.3	32	7.5
18	---	---	---
14	9.9	29	4.6
14	5.6	25	1.5
14	---	---	---
14	---	---	---
14	---	---	---
14	---	---	---
14	---	---	---
12	10.9	33	9.1
16	9.9	33	9.7
19	9.6	26	8.1
10	7.5	24	10.7
10	---	---	---
10	---	---	---
10	---	---	---
07	23.0	41	12.6
14	12.3	30	7.5
16	11.2	18	9.7
16	---	---	---
16	---	---	---
12	17.3	41	14.4
13	13.9	33	8.7
12	9.3	30	5.6
15	4.2	27	2.2
12	---	---	---
12	---	---	---
12	---	---	---
12	---	---	---
12	---	---	---
13	13.9	37	11.3
17	11.7	33	9.8
14	8.1	29	7.2
15	6.2	27	10.2
12	---	---	---
12	13.3	37	12.4
14	12.4	32	6.3
10	10.0	30	11.4
10	---	---	---

## APPENDIX B

### ENERGY SPECIFIC GASEOUS EMISSIONS INDICES (GR/BTU/KG BASE FUEL) AND THE COMBUSTION EFFICIENCY, CE, FOR THE TEST FUELS AT THE SELECTED OPERATING CONDITIONS

Table B-1 contains energy specific gaseous emissions indices and combustion efficiency for the test fuels at selected operating conditions.

TABLE B-1. ENERGY  
A

Fuel Description	Takeoff				Climb			
	THC	CO	NO <sub>x</sub>	CE	THC	CO	NO <sub>x</sub>	CE
Jet A Reference	1.6	14.3	6.2	99.6	7.0	36.1	4.7	99.07
JP-4 Base Fuel	0.9	12.5	7.0	99.74	4.4	26.3	5.9	99.40
JP-4 + 10% EtOH	0.2	11.5	7.5	99.80	---	---	---	---
JP-4 + 15% EtOH	1.1	14.1	6.5	99.67	6.5	29.3	5.7	99.27
JP-4 + 20% EtOH	0.2	10.9	7.0	99.80	---	---	---	---
JP-4 + 25% EtOH	1.5	15.0	6.1	99.64	8.3	31.1	5.3	99.18
JP-4 + 40% EtOH	2.0	17.4	5.4	99.56	12.1	36.2	4.7	98.95
JP-4 + 10% Aqueous EtOH + 3% SO-A <sup>①</sup>	0.1	10.0	7.9	99.83	---	---	---	---
JP-4 + 20% Aqueous EtOH + 3% SO-A <sup>①</sup>	0.1	10.2	10.0	99.79	---	---	---	---
JP-4 + 10% MeOH + 3% SO-A <sup>①</sup>	0.2	10.8	10.2	99.78	---	---	---	---
JP-4 + 20% MeOH + 3% SO-A <sup>①</sup>	0.2	11.8	10.18	99.75	---	---	---	---
JP-4 + 10% Aqueous MeOH + 10% SO-A <sup>①</sup>	0.2	14.4	16.5	99.69	---	---	---	---
JP-4 + 20% Aqueous MeOH + 20% SO-A <sup>①</sup>	0.6	19.3	24.4	99.51	---	---	---	---
JP-4 + 10% Clindrol 100 CG <sup>②</sup>	1.5	19.0	18.3	99.53	8.1	36.0	18.8	99.06
JP-4 + 5% H <sub>2</sub> O + 5% Clindrol 100CG <sup>②</sup>	1.9	18.8	13.0	99.53	10.1	42.0	11.8	98.83
JP-4 + 10% H <sub>2</sub> O + 10% Clindrol 100 CG <sup>②</sup>	5.0	28.6	18.3	99.12	25.3	67.2	17.5	97.66
JP-4 + 15% H <sub>2</sub> O + 15% Clindrol 100 CG <sup>②</sup>	9.5	39.8	24.2	98.65	44.6	92.8	22.6	96.34
JP-4 + 20% H <sub>2</sub> O + 20% Clindrol 100 CG <sup>②</sup>	1.0	23.8	30.5	99.28	---	---	---	---
Jet A + 0.01% Ferrocene	2.1	15.1	6.1	99.63	---	---	---	---
Jet A + 0.03% Ferrocene	2.3	16.1	6.1	99.59	---	---	---	---
JP-4 + 0.01% Ferrocene	1.1	12.1	6.8	99.73	5.7	31.8	5.5	99.25
JP-4 + 15% EtOH + 0.01% Ferrocene	0.8	11.7	6.1	99.72	7.8	35.0	5.1	99.10
JP-4 + 5% H <sub>2</sub> O + 5% Clindrol 100 CG <sup>②</sup> 0.01% Ferrocene	3.7	20.9	11.7	99.40	8.7	29.8	6.5	99.19
JP-4 + 15% EtOH + 0.1% Hydrazine	1.5	11.9	7.5	99.70	---	---	---	---
JP-4 + 15% EtOH + 0.6% Hydrazine	1.3	11.2	13.5	99.70	---	---	---	---
JP-4 + 15% EtOH + 0.01% Ferrocene + 0.1% Hydrazine	0.3	11.9	7.3	99.75	---	---	---	---
JP-8 Base Fuel	1.0	13.0	6.8	99.72	8.0	34.9	5.7	99.19
JP-8 + 10% EtOH	0.2	11.8	7.1	99.80	---	---	---	---
JP-8 + 15% EtOH	1.4	15.9	6.0	99.61	8.4	34.1	5.4	99.10
JP-8 + 20% EtOH	0.5	13.0	6.7	99.77	---	---	---	---
JP-8 + 25% EtOH	1.8	17.4	5.6	99.55	11.0	37.2	5.0	98.94
JP-8 + 40% EtOH	2.2	19.6	5.0	99.45	14.5	41.1	4.6	98.71
JP-8 + 10% Aqueous EtOH + 5% SO-A <sup>①</sup>	0.2	11.7	10.8	99.75	---	---	---	---
JP-8 + 20% Aqueous EtOH + 5% SO-A <sup>①</sup>	0.2	11.6	11.5	99.75	---	---	---	---
JP-8 + 10% MeOH + 6% SO-A <sup>①</sup>	0.4	12.6	11.8	99.72	---	---	---	---
JP-8 + 20% MeOH + 10% SO-A <sup>①</sup>	0.7	18.4	14.5	99.56	---	---	---	---
JP-8 + 10% Aqueous MeOH + 11% SO-A <sup>①</sup>	---	10.3	16.7	99.76	---	---	---	---
JP-8 + 20% Aqueous MeOH + 20% SO-A <sup>①</sup>	0.2	10.6	22.9	99.69	---	---	---	---
JP-8 + 10% Clindrol 101 CG <sup>②</sup>	1.1	11.0	16.9	99.71	6.7	35.4	15.7	99.06
JP-8 + 5% H <sub>2</sub> O + 5% Clindrol 101 CG <sup>②</sup>	2.2	16.4	12.0	99.58	13.7	44.7	10.5	98.72
JP-8 + 10% H <sub>2</sub> O + 10% Clindrol 101 CG <sup>②</sup>	2.7	24.7	16.0	99.33	22.8	69.4	14.9	97.83
JP-8 + 15% H <sub>2</sub> O + 15% Clindrol 101 CG <sup>②</sup>	4.0	31.3	20.4	99.06	33.5	89.0	18.5	96.95
JP-8 + 20% H <sub>2</sub> O + 20% Clindrol 101 CG <sup>②</sup>	0.3	18.9	26.8	99.44	---	---	---	---
JP-8 + 0.01% Ferrocene	3.5	15.5	6.2	99.60	8.3	35.2	5.3	99.12
JP-8 + 15% EtOH + 0.01% Ferrocene	1.9	16.7	6.0	99.61	10.0	39.6	4.8	98.98
JP-8 + 5% H <sub>2</sub> O + 5% Clindrol 101 CG <sup>②</sup> 0.01% Ferrocene	1.7	20.9	---	99.48	13.1	46.4	---	98.85
JP-8 + 15% EtOH + 0.01% Ferrocene + 0.1% Hydrazine	13.9	1.0	6.8	99.68	---	---	---	---

ENERGY SPECIFIC GASEOUS EMISSION INDICES (gr/Btu/kg base fuel)  
AND COMBUSTION EFFICIENCY (CE), %

CE	Cruise				Ground Idle			
	THC	CO	NO <sub>x</sub>	CE	THC	CO	NO <sub>x</sub>	CE
99.07	28.3	56.2	4.0	91.10	108.9	118.1	1.1	94.65
99.40	16.1	45.2	4.8	98.72	91.6	105.3	2.8	96.03
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99.27	25.0	52.9	4.4	98.49	154.9	133.0	2.6	93.94
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99.18	31.3	57.8	4.2	98.13	184.6	136.3	2.5	93.08
98.95	45.0	67.2	3.6	97.62	248.5	144.9	2.2	91.15
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99.06	24.4	63.0	18.1	98.05	136.6	135.2	14.0	94.04
98.83	37.4	72.1	10.5	97.41	141.8	122.7	5.8	93.47
97.66	69.5	97.8	14.9	95.73	292.8	153.1	9.2	88.49
96.34	128.6		19.6	93.69	532.1	193.2	10.8	80.82
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99.25	18.6	51.8	4.9	98.54	104.9	117.1	2.6	95.07
99.10	26.4	57.5	4.6	98.21	165.1	125.6	2.5	93.33
99.19	27.0	88.4	12.0	97.01	600.0	179.0	7.4	78.00
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99.19	24.4	57.8	4.9	98.41	122.0	128.2	2.7	94.32
---	---	---	---	---	---	---	---	---
99.10	29.8	56.5	4.1	98.16	197.8	147.9	2.4	92.34
---	---	---	---	---	---	---	---	---
98.94	35.9	61.1	3.9	97.87	242.3	155.4	2.2	90.94
98.71	52.0	74.3	3.3	97.11	288.5	156.8	2.0	89.80
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99.06	20.6	64.6	15.0	98.08	129.2	144.0	11.2	93.88
98.72	44.1	85.9	9.6	97.06	210.3	160.2	7.0	91.70
97.83	70.4	119.0	13.0	95.43	343.7	192.3	9.7	87.51
96.95	97.6	147.3	17.2	93.90	528.8	217.3	11.7	81.73
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99.12	20.6	56.9	4.1	98.40	96.2	122.4	2.4	95.19
98.98	36.7	70.2	3.6	97.45	193.9	126.9	1.5	92.30
98.85	37.2	78.6	---	97.19	159.6	135.9	---	92.61
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## INITIAL DISTRIBUTION

OASD(I&L)EES	1
OUSDR&E	1
OSAF/MIQ	1
DTIC/DDA	12
OSAF/PAM	1
HQ USAF/LEEV	1
USAFOEHL	1
USAFSAM/EDH	1
USAFSAM/VNL	1
AEDC/DOTR	1
USAF Hospital Wiesbaden/SGB	2
AUL/LSE 71-249	1
USAFA Library/DESEL	1
USAEHA, Ch, Env Chem Div	1
USA Med Bioengrg R&D Lab, Cmdr	1
AFATL/DLODL	1
SAALC/SFQT	1
Environmental Quality Division	
NAVFAC Code 112	1
NAPC/Code PE71:AFK	1
Library, Chemical Abstract Service	1
HQ AFESC/DEV	1
HQ AFESC/TST	1
HQ AFESC/RDV	1
AFWAL/POSF	1
AFIT/LSM	1
HQ AFLC/DE	1
HQ AFLC/DEPV	1
HQ AFLC/IGYG	1
AFOSR/NA	1
FAA/AEQ-10	1
HQ AFESC/RDVC	5
Southwest Research Institute	3
Secretary of the AF (SAFRD)	1
USAF/AFRD	1
AFATL/DLODR	1